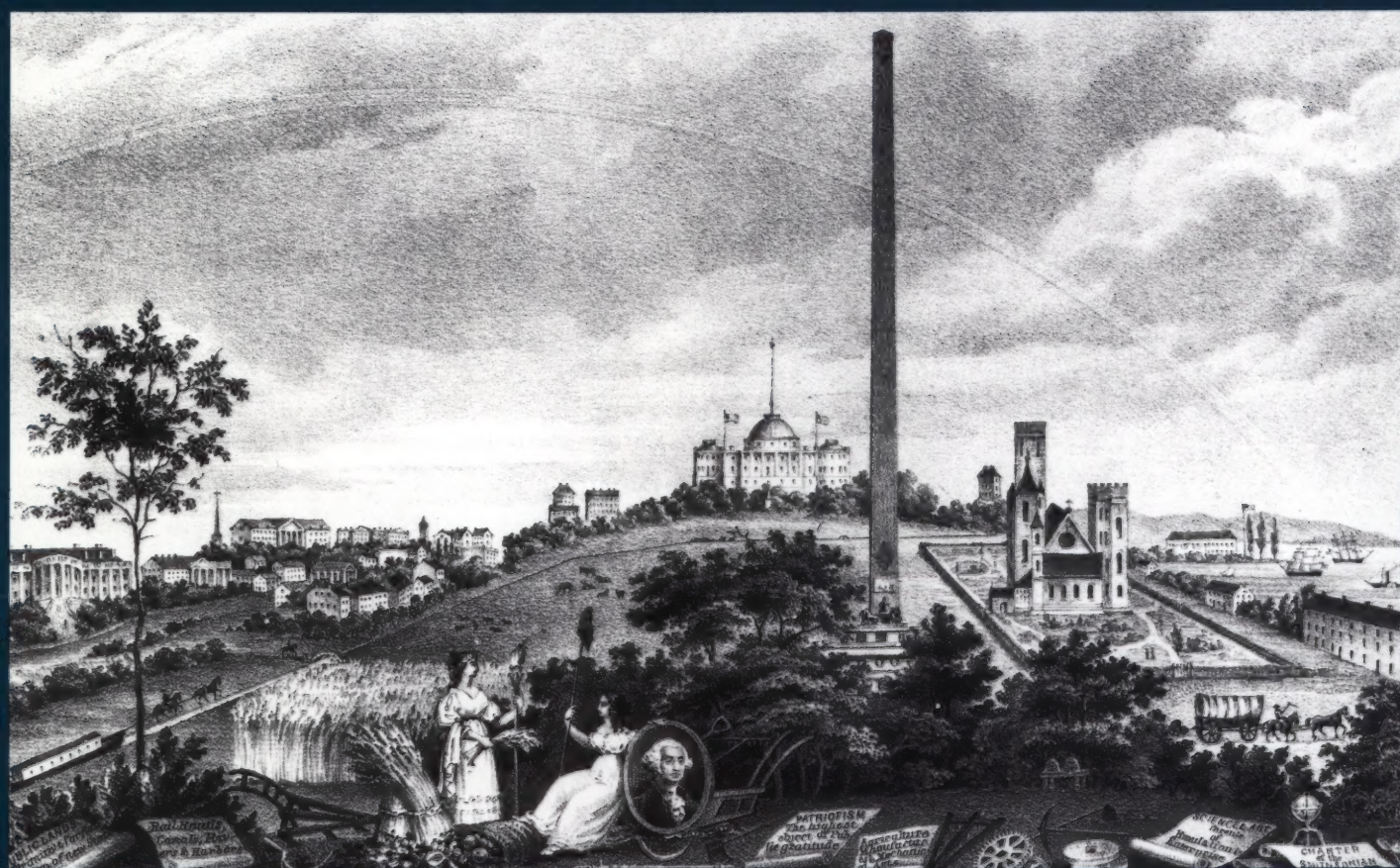


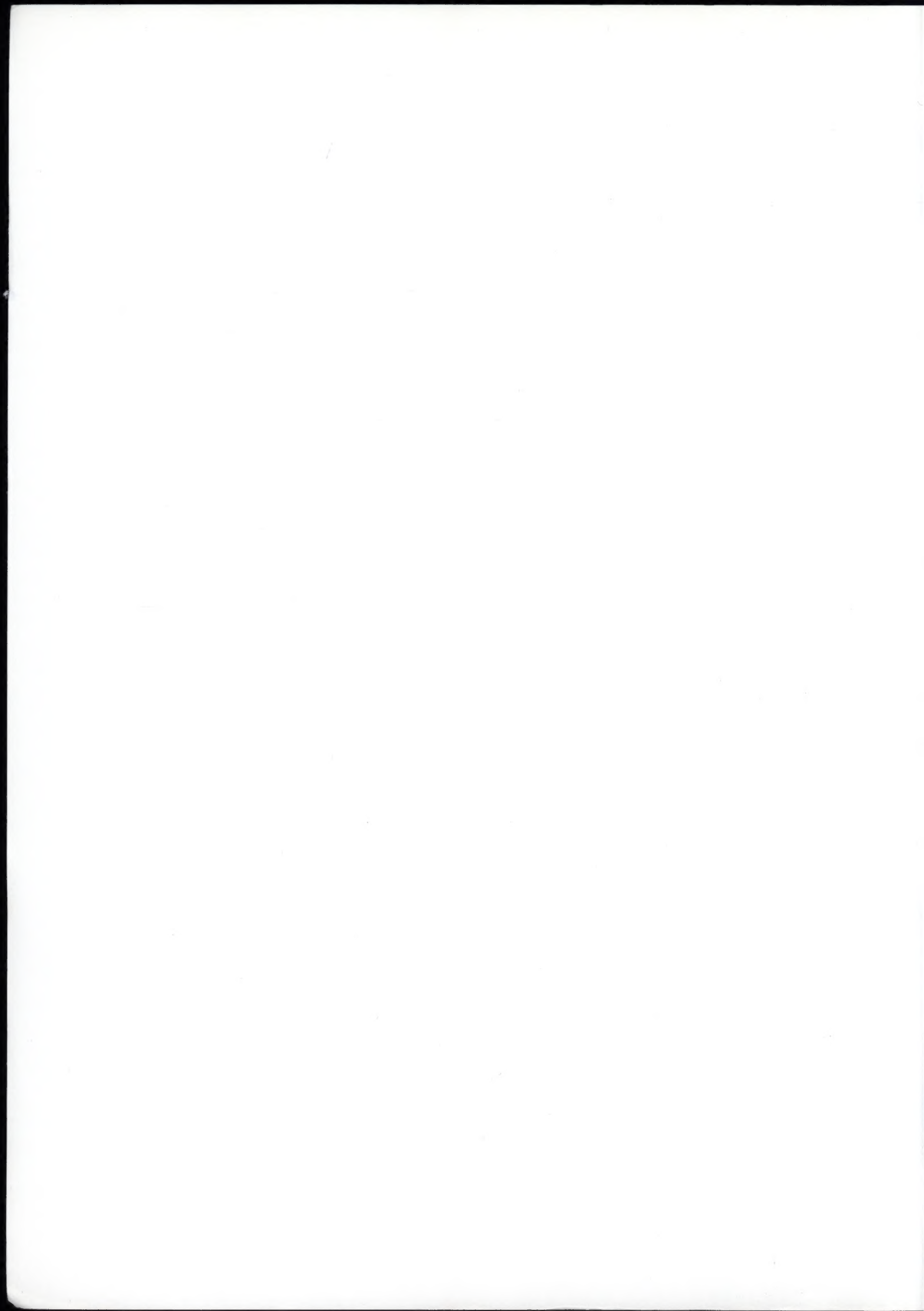
ICOM COMMITTEE FOR CONSERVATION

10th Triennial Meeting
Washington, DC, USA
22–27 August 1993

Preprints Volume II



COMITÉ DE L'ICOM POUR LA CONSERVATION



COMMITTEE ON CONSERVATION

REPORT

ON THE

PROGRESS OF THE

COMMISSIONERS OF THE GENERAL LAND OFFICE

IN THE YEAR 1847

AND THE

LANDS OF THE

REVENUE

IN THE YEAR 1847

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A NOTE ON THE COVER

"Elements of Thrift and Empire:
Public Lands, Railroads, Canals
and Harbors; Agriculture,
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Arts; Science and Art, the Parents
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Lithograph by E. Weber & Co.,
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ICOM COMMITTEE FOR CONSERVATION
Preprints 1993

Editor's Note/Note de la rédaction

This edition of the Preprints marks the advent of a computer-based production system to replace the grid sheets that have been used in the past. While this has resulted in a more uniform and aesthetic publication, the introduction of these new procedures has held many challenges. Among these have been time constraints that have prevented a final review of text or layout by the authors. Nonetheless, I hope that they and all who consult these Preprints will be satisfied with the end result.

Another new feature of these Preprints is the inclusion of abstracts from the poster session of the 10th Triennial Meeting. The abstracts are arranged here in the order in which they appear in the poster session, rather than by Working Group.

I would like to thank the Working Group Coordinators and the authors for their co-operation and support throughout the preparation of these volumes. A special vote of thanks is due to the members of the Preprints Committee, who gave so generously of their time and energy, not only in reviewing the submissions with such diligence, but also through their assistance during the subsequent editing process. Finally, I am grateful to the editors of the poster abstracts for proposing and undertaking this complement to the Preprints.

Cette édition des prétrages marque une étape, celle de l'informatisation du système de production, accompagnée de la disparition des grilles utilisées auparavant. Si, en conséquence, l'aspect de la publication est plus uniforme et esthétique, l'introduction de ces nouvelles procédures a présenté de nombreux défis. On peut trouver à leur nombre des contraintes de temps qui n'ont pas permis aux auteurs de procéder à une révision finale des textes ou de la mise en page. J'espère toutefois que les auteurs aussi bien que tous ceux qui consulteront ces prétrages seront satisfaits du résultat final.

Une autre innovation du système est l'inclusion des résumés de la séance des panneaux d'affichage de la 10ème réunion triennale. Les résumés sont arrangés ici dans l'ordre de la séance plutôt que par groupe de travail.

Je voudrais remercier les Coordinateurs des groupes de travail ainsi que les auteurs de leur coopération et leur soutien au cours de la préparation de ces volumes. Un vote de remerciements s'adresse tout spécialement aux membres du Comité des prétrages qui ont si généreusement consacré leur temps et énergie non seulement à la révision diligente des textes qui leur étaient soumis, mais aussi au travail d'édition qui en découlait. Je voudrais enfin exprimer ma reconnaissance aux éditeurs des résumés des panneaux d'affichage pour avoir proposé et mené à bien ce complément aux prétrages.

—J.B.

ICOM COMMITTEE FOR CONSERVATION

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Working Group 14

Graphic Documents

Documents graphiques



Abstract

Examination and conservation treatment of a rare, oversized, 16th-century Mexican Indian pictorial map on amate paper are described. The map is a complex written and pictographic record in Spanish and Nahuatl concerning a dispute of land ownership in Texcoco, part of the triumvirate of Mexico City during the Spanish conquest. Examination of the map included a study of the fibers and the pigments, a record of the condition of the map, as well as a comparison to another 16th-century Aztec codex in the Library of Congress' collection. Conservation treatment of the map involved consolidation, reversal of two previous lining treatments using a Goretex® humidification treatment, washing on wet blotters and the suction table, and filling the extensive wormhole damage using a pulp made from modern hand-made amate paper.

Keywords

Amate, paper, oztoticpac, Aztec, Nahuatl, conservation, pulp fills, Goretex® backing removals, blotter-washing



Figure 2. Detail, after treatment. Glyph for the estate of Oztoticpac, which corresponds to the "above the caves" (oztoitl, cave; icpac, above) a hill stylized in the shape of a woman. Depiction of tree grafts shows European fruit tree branches grafted to indigenous tree trunks.

The Oztoticpac Lands Map: Examination and Conservation Treatment of a 16th-Century Mexican Map on Amate Paper from the Library of Congress

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Examination

Background and Provenance

Library of Congress records indicate that the Oztoticpac Lands Map (figure 1) was received by the Geography and Map Division in 1965 from the Government Printing Office, newly mounted onto 'rag' paper, backed with heavy cotton fabric. (1) Unfortunately, at present there are no other known records of the map's provenance. In 1966, an in-depth article was written by Howard Cline, then Director of the Hispanic Division at the Library of Congress, placing the map in its historical context and interpreting its language and pictographs. (2)

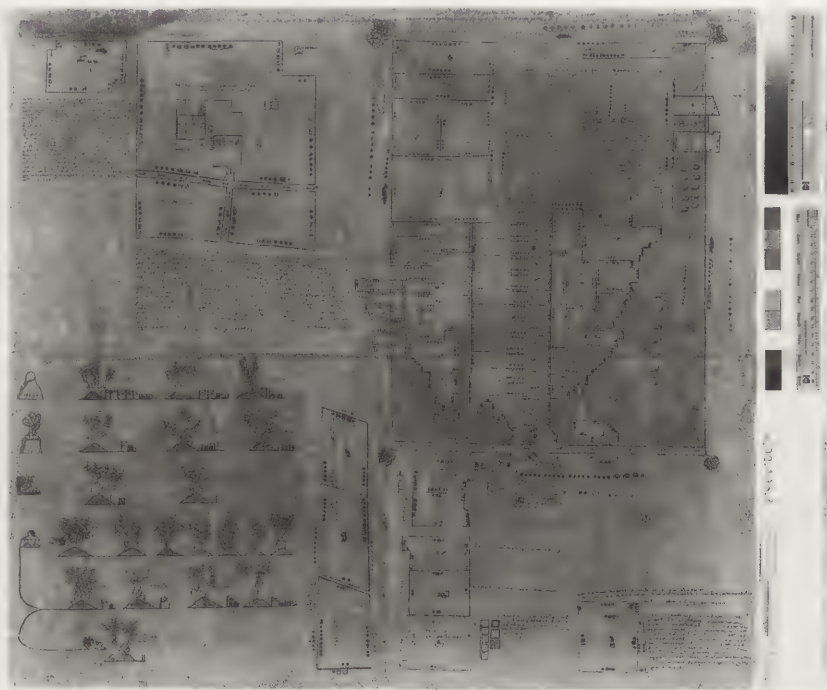


Figure 1. Oztoticpac Lands Map. After conservation treatment.

This fascinating analysis reveals much of the map's content and remains a primary source of information on the piece. Characters depicted and/or discussed in the Oztoticpac map include a number of well-known figures in 16th-century Mexican history such as: Nezahualpilli, the Texcocoan king; Hernando Cortés and Pedro Alvarado, the Spanish conquistadores; Bishop Juan Zumárraga, the Inquisition official; Bernardino de Sahagún, the missionary; and, Antonio de Mendoza, the first Viceroy. "A climax and raison d'être of the document comes with the execution of a Texcocoan noble (son of Nezahualpilli) in the public square of Mexico City before an assemblage of Spanish and Indian notables and commoners." (3) The subsequent dispute over the land owned by this unfortunate character is recorded on the Oztoticpac Lands Map. (figure 2)

Condition of the map

The map consists of two layers of Mexican amate handmade paper adhered together, measuring 83cm × 75cm. There are four kinds of drawing media on the document, done by what looks like four different scribes. The principal



Figure 3. Detail, showing the amate paper and its two backings: paper and fabric.

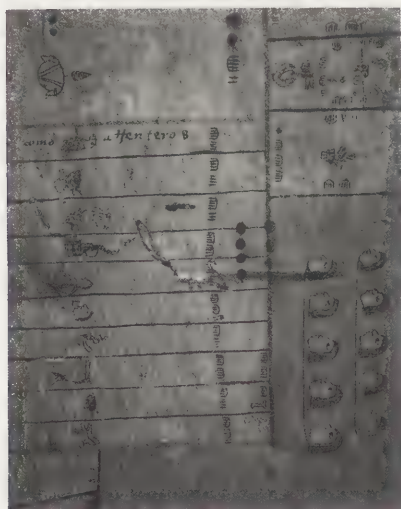


Figure 4. Detail showing delaminating condition.

diagrams of the map were done by one or more Indian scribes and were drawn in black. An interpreter added a number of glosses in transcribed Nahuatl. Nahuatl numerals are present in red and there are shorter Spanish glosses written in black. Across the top of the map is another Spanish inscription, by a different hand, in brown ink.

The map was subject to repeated handling after its 1965 lining and the support did not prevent flexing of the original. The flexing caused splitting and breaking of the amate (figures 3,4). Although thick, the amate was only loosely held together as a fiber sheet. Many serious breaks, tears, and delaminations appeared in it which were not present in the Library's publication photographs of 1965. (4) The entire map could not be handled without causing further damage.

The surface of the map was quite distorted and soiled. This was in part from exposure to light and airborne pollutants, but also indicates heavy use and handling at some time in the document's history. Accretions and stains were visible on the map's surface. The paper was very dark in color compared to another amate document in the Library's collection: the Huejotzingo Codex. (5) Microscopic comparison of fiber samples from Oztoticpac with those of the Huejotzingo Codex amate fibers, indicated the fibers were very similar, if not the same. (6) Under the large tears which exposed the delaminating interior, the fiber was much lighter in color. No lignin was present in the paper. (7) Local tests indicated that a considerable amount of yellow discoloration present in the paper released easily with water. The surface pH of the paper was measured with ColorpHast Indicator Strips® and found to be 3.5–4.0.

The mounting had been done with an orange adhesive, applied thickly and unevenly, such that it was visible through the cotton fabric. The adhesive gave a positive test for both starch and protein. (8) There were numerous wormholes in the amate which were present before the backing was applied. These had been filled later with tinted Japanese papers in the 1970s by a Library of Congress conservator, in order to tone down the bright white of the backing and minimize the visual interference of the holes. Prior to lining the map had been folded into eighths or more, and the creases were visible on the recto and the verso, under the lining. The creases were opened up but not sufficiently flattened when the map was lined. It is clear that heavy pressure was exerted on the surface of the map to attach the lining. The original paper texture was much flattened. Other 16th-century amate paper examined by the author has a texture of parallel ridges like corduroy fabric, left as an imprint of the pounding stones used to make the paper. (9) Here one still sees the ridge lines but they are no longer raised.

On the recto, along the creases, the paper exhibited serious damage and the media was distorted. The fibers were broken and very brittle all along these areas and any amount of flexing risked loss of information. Some of the very small writing in these areas was not very legible because the local areas were distorted from the creases. It was not possible to properly flatten and align design and text areas without removing the backing.

Repairs of some of the delaminating areas had been done with a resinous material which had become brittle and no longer functioned as an adhesive. Along the top edge, the fibrous paper was barely holding together, and the writing was in danger of being lost altogether. Local reattachment of the delaminating areas and consolidation were necessary to preserve what was already compromised by the condition of the paper.

Condition of Pigments

Under polarizing light microscopy the red pigment appeared identical to the vivid red cochineal of the Huejotzingo Codex. (10) However, under normal viewing conditions, the red designs of the Oztoticpac map were very dull and dark in comparison. The local application of a small amount of water on the red areas under the microscope saturated small very bright red crystals and brightened the overall color markedly. When the moisture dried, the red pigment became dull and dark again. It is clear that the colorant has deteriorated

considerably with age as well as exposure to light and atmospheric pollutants. The black ink appears to be carbon-based and is in good condition overall. The one brown ink inscription appears to be iron-gall and is both faded and physically distorted by the losses in the upper edge of the paper. During close examination, a stripe of light-colored pigment was discovered all along the black outlined footpath around the land plots. This stripe has severely faded and is not immediately visible. The color is more visible as an orange-brown under ultra-violet visible reflectance, but it is not clear what color it originally was in daylight. Further analytical tests are currently in progress.

Conservation Treatment Record

Photodocumentation

The map was fully documented with 35mm color slides and 10 × 12.5cm format color transparencies as well as black and white prints before and after treatment. Color slides of the treatment process were also taken.

Physical Stabilization

Delaminating areas of the map had to be consolidated before any removal of the backing could begin. The lifting areas were set down with Methocel® A 4M 1% in water. The adhesive was applied to paper strips supported by Mylar® tabs and then inserted under the lifting flaps. A dental spatula was used to hold up the original while the Mylar support was inserted underneath, pressure from the top was applied and then the Mylar and paper slowly pulled out from underneath. Areas which required topical consolidation were coated with Methocel® A 4C 1% in water and alcohol 1:1, and then locally weighted. This solution penetrated the amate paper layers well without discoloring the surface. The edges of the map in particular required a considerable amount of consolidation and re-attachment.

Multiple tests to find an appropriate facing material did not produce desirable results. Experiments were carried out with dilute solutions of BEVA 361® adhesive, Lascaux 360®, and Rhoplex N580® coated onto Japanese tissue, and also Filmoplast P® tape, and LC Heat-Set tissue. Each of these test materials was cut into small strips and applied to a piece of modern painted amate, and then removed, using solvents or heat, where appropriate. None of the above systems effectively solved the problem of holding the surface together without picking up friable media when removed. (11) No material could be found which did not pick up some small amount of media, therefore no facings were employed during the treatment.

Backing Removal

After consolidating the front and setting down the lifting areas, the map was turned upside-down and the secondary linen fabric backing was removed mechanically. This revealed the U.S. Government Bond watermarked paper used as the primary backing. The removal of the paper backing proceeded much more slowly (figure 5). A Goretex® and wet blotter sandwich was used in local areas for two hours or more in order to soften the adhesive layer enough to pull off the backing paper. Layers in the sandwich were as follows:



Figure 5. Removing the paper backing.

TOP
Felt and Plexiglas® weight
Polyester sheet
Wet Blotter
Goretex® sheet with felt side against the blotter
Map, face-down
Goretex® sheet, smooth surface against the map
Wet blotter
Polyester sheet
BOTTOM

Using the Goretex® on the recto of the map image prevented too much moisture from coming through the blotters and disturbing the pigments. The dental tool

aided in separating the backing paper from corners, edges, and where strongly stuck due to unusually thick layers of adhesive. The fibers became a little fuzzy and rough in some areas due to the quantity of adhesive applied and the previously worn character of the paper in those areas. One particular area was more worn than the rest because it had been the exposed part of the paper when the map had been folded into eighths. The recto was undisturbed. After the backing paper was removed, a substantial amount of adhesive remained lodged in the fibrous paper. The adhesive was thick and not easily dissolved. It could not be swabbed off due to the fibrous nature of the paper. Any rubbing of the verso disturbed the paper fibers.

With the verso amate layer now exposed, one could see that this layer was made of four overlapping pieces of paper. The recto, on the other hand, was made of only one piece. The verso and recto papers were also different colors.

Washing

Blotter-washing experiments were carried out on small parts of the removed backing papers which were still covered with adhesive. These tests revealed that several layers of smooth thin blotting paper placed directly against the adhesive layer removed the largest quantity of adhesive. Interleaving layers such as Hollytex® polyester web interfered with the absorption of adhesive into the blotter. Other thicker or more textured blotting papers did not provide adequate, even contact and removed an uneven quantity of the adhesive. An enzyme solution composed of a mixture of alpha amylase (Sigma No. A6380 Type II-A, concentration: .1g/l) and trypsin (Sigma No. T-0134 Type IX, concentration: .1g/l) deposited in the blotter pulled out the most adhesive by far. (12) Neutral water-soaked blotters and alkaline water-soaked blotters also effectively reduced the adhesive layer with three or more changes of blotter but not as well as the enzyme solution. Upon further testing, however, it was decided to forego using the enzymes due to the fragility of the media and the unlikelihood of removing all enzyme solution residue from the paper even with rinsing. The media and paper could only undergo limited amounts of water exposure, and the paper retained moisture for a very long time. Complete drying occurred only over several days. Placing the map directly on the blotters soaked with an alkaline water solution was selected as the safest and most reasonably effective method for washing.

The map was humidified between Hollytex® and Goretex® layers and wet blotters for 1/2 hour while the sink was prepared for washing.

A Mylar® film was placed at the bottom of a large metal tray. Two layers of blotting paper were generously wet out over thicker blotter, using deionized water with calcium hydroxide solution added to pH 8.0–9.0.

The map was positioned between Hollytex® sheets onto a rigid support and then slowly brushed onto the wet blotter with a Japanese brush (figures 6,7), rolling the Hollytex® sheeting around the back of the cardboard and releasing the map very slowly. The amate paper had expanded considerably and was too weak to be handled without a support. Careful positioning was necessary in order to lay the paper down in even contact with the blotters.

After positioning the map on the wet blotters, it was sprayed from the top with 1:1 water : alcohol in order to wet out the amate evenly. Corners were lifted with Mylar® support on the top to re-position with a brush when crooked or wrinkled. The entire metal tray was covered to prevent surface drying and the map was left in place for 45 minutes. The blotters became very discolored.

The map was then removed from the tray as a whole package, lifting the Mylar® support under the blotters. The whole package was sandwiched between rigid boards and then flipped over. Blotters were peeled away (figure 8) and new wet blotters prepared. The map was set down in the same way as before. Three 45-minute washes were done in all. After the second and third 45-minute wash, the adhesive on the verso was reduced by working on the map upside-down. Cotton swabs and blotters were applied and stroked through bridal veil netting stretched on upholstery hoops to pull out adhesive without lifting up the fibers.

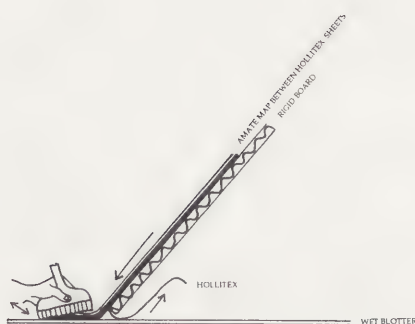


Figure 6. Diagram illustrating method for positioning map onto wet blotters with no interleaf.

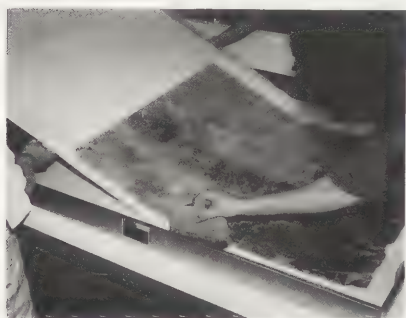


Figure 7. Brushing map onto wet blotter for washing.

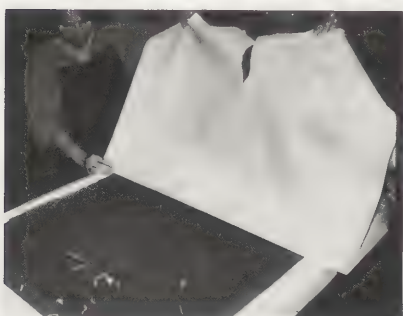


Figure 8. Discolored blotter after first wash.

After the third washing, the map was put on the suction table and spray-washed once with alcohol:water 1:1, and once with pH 8.0 water over blotting paper. This technique was not as effective as the wet blotter in removing discoloration. The blotters became discolored but not very evenly. Small black spots began to appear in the blotter below. Because the medium was slightly sensitive when wet, this technique was abbreviated and the map was placed between Hollytex® and thick felts and dried for one week.

After drying, the amate appeared much lighter in color and the media brighter and more legible. The flexibility of the paper was somewhat improved. Much adhesive had come out of the paper though some was still present on the verso. The amate paper layers were fairly well adhered and no overall sizing seemed necessary. Some local sizing and reattaching of delaminating areas was done with Methocel® A 4M 1% adhesive, which could be more liberally applied without staining, after the washing treatment.

Further attempts to remove the adhesive locally from the verso were not successful. Enzyme poultices applied to the verso affected the media on the recto adversely and stained the paper. Local rubbing was impossible due to the fibrous nature of the paper. Because the map was in two layers and the adhesive did not seem to have penetrated the recto, at least visually, it was decided to leave the residue as it was without carrying the treatment further.

Mending

Amate paper pulp was prepared from samples of small sheets of modern previously handcrafted amate made in the traditional method. (13) Sheets were cut up and soaked overnight and cooked for one hour and then put into a blender.

The pulp was colored with acrylic paints, drained and dried overnight, then re-hydrated in a blender. This step prevents bleeding of the color into the water solution and subsequently into the original map. The tone selected matched the recto, and was therefore more visible on the verso.

Pulp was blotted, small clumps at a time, and then applied over a light box to the areas of loss (figures 9,10,11). The fills were shaped and molded to fit the wormholes using tweezers and spatulas. After further blotting, weighting and drying, the pulp shrank a little and required an additional layer. Some of the larger holes were filled from both sides.

Edge holes beyond a certain size were filled with pieces of amate paper cut with a stylus to fill the size of the loss and toned with acrylic paints. Wheat starch paste was used to attach these. All fills, weak areas and creases were reinforced with *tengujo* Japanese tissue from the verso.

After drying, the fills on the recto were adjusted in color with colored pencils. Fills are easily distinguished from the original on the verso. The pulp fills and Japanese paper mends returned an overall stability and physical integrity to the map which rendered a new lining unnecessary.

After conservation treatment, the Oztoticpac Lands Map was displayed as part of the Library of Congress Quincentenary Exhibition: "An Ongoing Voyage, 1492-1992", where it received considerable attention (see figure 1). Its permanent storage is a sink mat with a rigid support which does not allow the map to be flexed, and a Mylar® covering which is not in direct contact with the surface.

Conclusions

Codices and other amate documents which have been mounted onto unsuitable supports suffer damage to their physical well-being as well as altered appearances. It is possible with care to reverse these treatments, though residues of the former treatments may remain. It is important to consider how far to go with one's own treatment in order to preserve the document in question without inflicting any further damage. Controlled blotter-washing can be more successful with papers such as amate than the suction table. Traditional papermaking techniques using modern amate fiber can make appropriate pulp fills for older amate doc-

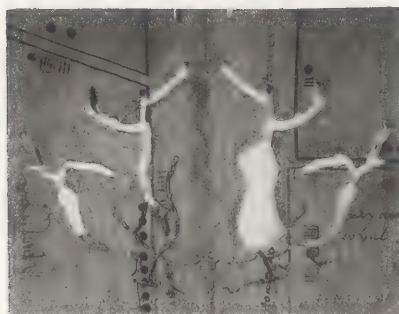


Figure 9. Detail, after washing, showing wormholes.



Figure 10. Pulp filling.

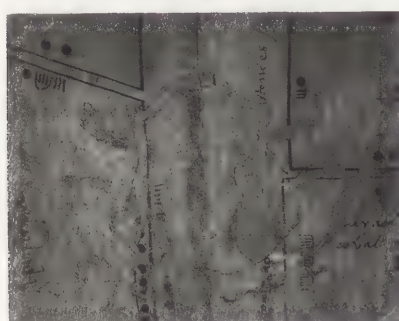


Figure 11. Detail, same as figure 9, after treatment.

uments. None of the tried adhesive formulations made a successful facing material for this document.

Acknowledgements

I would like to thank my colleagues at the Library of Congress for their assistance in this treatment project, especially: Rachel Danzing (NYU graduate intern 1992), Heather Wanser and Ann Seibert, Senior Paper Conservators, and Merrilee Oliver, Photographer.

Notes

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2. Ibid., 75-115.
3. Ibid., 77.
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7. B.L. Browning, *Analysis of Paper* (New York: Marcel Dekker, 1969): 65.
8. Ibid. 83, 95.
9. Albro, *Op. cit.* 105.
10. Ibid. 101, 105.
11. An outline of these experiments could not be included here. For further information on these experiments please contact the author.
12. J. Segal and D. Cooper, "The Use of enzymes to release adhesives," *The Paper Conservator, Journal of the Institute of Paper Conservation*, 2 (1977): 47-50.
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Materials

ColorpHast Indicator Strips: E. M. Science, 480 Democracy Road, Gibbstown, N. J. 08027 USA.

Methocel® A 4M, A 4C: Dow Chemical Company. For Product information and samples: 1(800) 258-2436.

BEVA 361®, Lascaux 360®, Rhoplex N580®: Conservation Materials, 1165 Marietta Way, Sparks, Nevada 89431 USA.

Filmoplast P®: Hans Neschen GmbH & Co. KG, D-3062 Bückeburg, Germany.

Goretex®: W. L. Gore and Associates, 100 Airport Rd. Box 1550, Elkton, MD 21921 USA.

Alpha Amylase A6380 Type II-A: Trypsin T-0134 Type IX: Sigma Chemicals, P.O. Box 14508, St. Louis, MO 63178 USA.

Hollytex®: Talas, 213 W. 35th St., New York, N.Y. 10001 USA.

Amate fibers/Moracea fibers: Lee Scott McDonald, P. O. Box 264, Charlestown, MA 12129 USA.

Tengujo tissue: Paper NAO, 1-29-12-201 Sengoku Bunkyo Ku, Tokyo 112, Japan.

Abstract

The results presented in this paper are the outcome of a project investigating the ageing behavior of several modern types of papers after preventive deacidification and restrengthening treatment. The project was conducted at the facilities of the Austrian National Library in Vienna. Included in the research program were samples treated with other mass preservation techniques, such as the DEZ-process or the FMC-Lithco method using MG-3 as the deacidifying agent. Special consideration was given to the short-term and the long-term behavior of the deacidified papers towards acidic and/or oxidizing atmospheric pollutants such as SO₂ and NO_x at a constant relative humidity of 65%. The concentration of SO₂ for short-term exposure was 130 ppb, and 208 ppb for long-term treatment. The respective concentrations for NO_x were 315 ppb and 422 ppb. The project is not yet completed; the first results describing the uptake of pollutants are given.

Keywords

Paper preservation, mass deacidification, modern paper, gaseous pollutants, absorption

Effects of Atmospheric Pollutants on Deacidified Modern Papers

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Introduction

The most significant factors for paper decay are a result of acid contamination of paper from either endogenic factors, e.g., acid pulping or acid sizing, or exogenic influences such as oxidation of cellulose or uptake of atmospheric acidic pollutants by cellulose containing materials. Acid catalyzed deterioration causes 80–90% of the paper decay in libraries and archives (1). As a result, libraries have initiated programs to develop new technologies. Primarily deacidification treatments of routine library materials on a mass scale have been developed, in addition to the traditional conservation efforts to treat individual precious items.

Mass deacidification techniques must be regarded as preventive conservation techniques. The goal is to inhibit or at least slow down acid decomposition of endangered paper items. Very little is known about the long-term stability of deacidified single paper items, and even less is known about the permanence to be expected if whole books have undergone mass-deacidification treatments. The permanence of the alkaline reserve which is deposited within the treated items is particularly important, as any developer claims permanence of the introduced alkaline reserve. The alkaline earth carbonates, zinc oxides, or magnesium/titaniumcarbonates/oxides are expected to increase "the life expectancy" of the treated item. This is contradictory to recent results published by Daniel, Flieder, and Leclerc concerning the consumption of different compounds deposited as alkaline reserves in paper under the influence of atmospheric pollutants such as SO₂ and NO_x (2, 3).

The goal of the current research project is to evaluate the efficacy of the "Viennese Method" for the preservation of newspapers based on an aqueous immersion treatment in a solution of calcium hydroxide and methylcellulose (4, 5). Other deacidification procedures on a mass scale have been included in order to be able to rank the competing technologies according to their ageing characteristics. Regarding the results of Daniel, Flieder, and Leclerc, consideration was given to investigating the behavior of deacidified book blocks of selected modern papers when exposed to gaseous atmospheric pollutants (2, 3).

Experimental

Specification of the facility for simulating pollution of paper blocks

The facility set up for evaluating the effects of atmospheric pollutants such as SO₂ and NO_x under constant relative humidity (RH) on deacidified paper with online gas analysis consisted of two parts: one for the investigation of short-

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term exposure with 8 treatment chambers and a second part for long-term exposure with one treatment chamber.

The two exposure units were built separately so that their parallel use could be possible. The basic construction difference between the two facilities was the kind and number of exposure chambers comprised, as well as the analytical devices present in the facility. By the short-term exposure method, the absorption of pollutants was measured within the first 24 hours. By the long-term exposure method, the total absorption of pollutants into paper samples in block form was analyzed within one month.

The apparatus was based on an atmospheric corrosion testing facility originally developed for examination of the corrosion behavior of metal or stone artifacts (6). It was modified for application to paper samples—small adhesive bound blocks or single leaves—by L. G. Johansson in 1989 (7). It consisted entirely of glass and Teflon (R), and its main advantages were high accuracy in control and regulation of temperature, gas flow, RH, and concentration of gaseous pollutants.

Principle of the long-term exposure facility

The construction of the long-term exposure facility and the method to create a defined polluted environment are represented, in principle, in Figure 1.

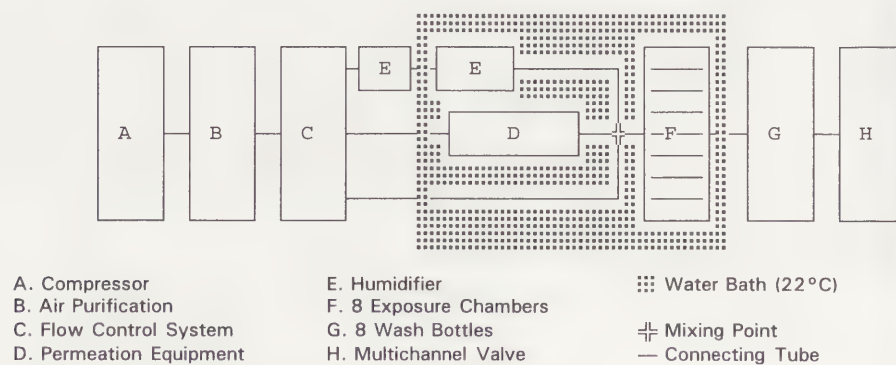


Figure 1. Sketch of the long-term exposure facility.

The compressed air from the compressor (A) passed an air purification unit (B), where contaminants such as NO_x , SO_2 , H_2O and organic impurities were removed. After that it was dispatched to the gas current control (C) where the air flow was separated into four different subflows. The dry purified air flow ($\text{RH} = 0\%$), was led directly to the mixing unit. The second flow passed through the humidifier (E) to become saturated with water vapor (100% RH). The other two gas flows were used as carriers for the gaseous pollutants. SO_2 and NO_x , respectively, were added to the dry air flows with thermostated permeation tubes (D) containing the liquified gases. At constant temperature, the tubes introduced the respective components to the air stream at a constant rate. The four gas streams were mixed and thermostated. The resulting concentrations of pollutants were 208 ppb SO_2 and 422 ppb NO_x . The 65% RH was obtained by mixing definite amounts of dry and humidified air.

The polluted and humidified air stream passed through the eight exposure chambers (F). The samples were fixed by means of nylon threads with a thickness of 0.1 mm—which do not themselves absorb SO_2 —through a hole in the upper part of every sample. Finally, the gas flow passed to a wash bottle (G) containing a 1% H_2O_2 solution in order to bind the total amount of SO_2 which was not taken up by the samples under investigation. In order to estimate the quantity of SO_2 absorbed by the paper blocks, the sulfate concentration of the solutions in every washing bottle was determined. This was performed through titration with $\text{Ba}(\text{ClO}_4)_2$, using a thorine-indicator (8). The resulting value represented the uptake of SO_2 by the respective paper block with consideration of the total quantity of SO_2 that passed through the exposure chambers during the measuring time.

After the absorption containers (G), the channel control valve (F) was mounted, which leaves the air flow running for 15 seconds through each of the exposure chambers. D, E and F were placed inside a water tank that is thermostatically adjusted to 22 ± 0.03 °C. The duration of sample exposure was 28 days.

Principle of the short-term exposure facility

The construction of the short-term exposure facility and the method to create a defined polluted environment is represented, in principle, in Figure 2.

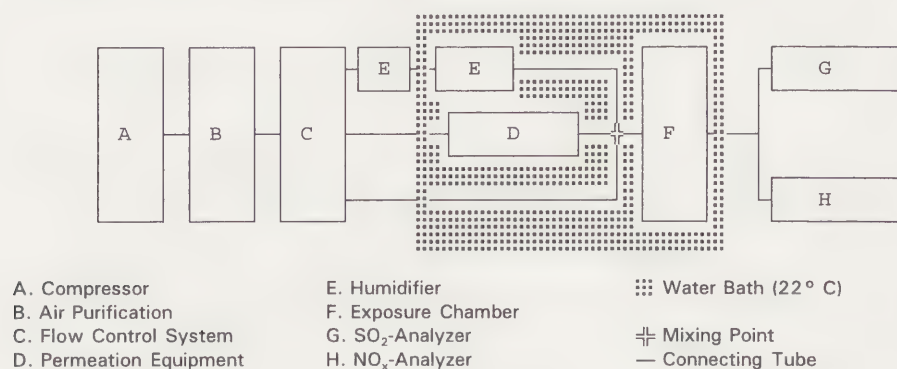


Figure 2. Sketch of the short-term exposure facility.

The compressor (A) and an air purification unit (B) were identical for both installations. From the gas current control (C) onwards, the two systems were separated, but they basically consist of the same units. One air flow passed through the humidifier (E) to become saturated with water vapor (100% RH). The dry air stream served as a carrier for the gaseous pollutants. SO₂ and NO_x, respectively, were added to the air flow with thermostated permeation tubes (D) containing the liquified gases. For technical reasons, the concentration of pollutants in the short-term exposure system was lower than the one in the long-term exposure facility. The gas flows were mixed and thermostated. The resulting concentrations of pollutants were 130 ppb SO₂ and 315 ppb NO_x, and the 65% RH was identical to the long-term exposure unit. The gas stream passed through the exposure chamber (F)—just one in this system—and was continuously analyzed after leaving the exposure chamber for SO₂ and NO_x. The SO₂ was analyzed with a ML Fluorescence SO₂ Analyzer Mod. 8850 (G), and the NO_x with a chemifluorescence analyzer (ML Nitrogen Oxides Analyzer Mod. 8840) (H). The detection limits for SO₂ and NO_x were 0.001 and 0.002 ppm, respectively. The uptake of pollutants by the samples under investigation was calculated from the concentrations measured before and after the exposure. Any effect of pollutant absorption by materials on the equipment therefore can be ignored. The duration of sample exposure was 24 hours.

Samples

The following four different types of paper of Austrian origin were examined during the first step of this project:

- Neusiedler, BIOTOP 3, 80 g/m², 100% chlorine-free bleached sulfite pulp, 10–15% CaCO₃ filler, rosin size mixed with starch—neutral, permanent according to Austrian Standard A-1119
- Wiener Papier FEDERLEICHT, 80 g/m², 100% sulfite pulp, chlorine bleached, 5% clay and CaCO₃ filler, rosin size—neutral, traditional book paper
- Zweckform RECYCONOMIC COPY, 80 g/m², 100% recycled paper
- 50% household waste paper medium quality, rosin size—acid, surface sizing with degradable potato starch
- Leykam ZEITUNGSROTATIONSPAPIER (NEWSPRINT), 50 g/m², 60% recycled paper, 40% groundwood, 5% clay filler plus small amount of CaCO₃, rosin size—neutral, newsprint.

For the selection, consideration was given to products which are advertised as

permanent according to the Austrian Standard A-1119 such as BIOTOP 3, or paper qualities which are politically recommended for use due to ecological reasons such as RECYCONOMIC COPY (9).

The paper samples were prepared as book blocks in A5 format with a spine height of 1 cm, using routine adhesive binding, but omitting cover boards. Identical samples were sent for deacidification treatment to Akzo (DEZ) (Texas Alkyls Run Number 58, 18.-21. 08. 1991), FMC-Lithco (MG-3), and the National Library of Austria (aqueous solution of $\text{Ca}(\text{OH})_2$ /methylcellulose; = ÖNB).

For testing the effects of gaseous pollutants, the paper samples were prepared from the book blocks in the general format of 145mm length and 15 mm width. The spine height was generally 1 cm. According to variations in thickness or weight/m², blocks of unlike papers consisted of a different number of sheets.

Test Procedures, Results and Discussion

All tests were performed on untreated reference materials, artificially aged samples, papers after deacidification treatment (FMC, ÖNB, DEZ), and deacidified papers after short-term or long-term exposure to polluted air under the conditions described above.

The artificial ageing was performed on freely hanging block samples in a climate chamber. The ageing conditions were 80°C and 95% RH, maintained continuously. In order to gain insight into the progress of ageing phenomena of the tested papers, samples were taken for determination of their mechanical and chemical properties after 1, 2, 4, 8, 16, and 32 days of ageing.

Standard test procedures were used to evaluate folding endurance (DIN 53412), tensile strength (DIN 53112A), and bursting strength (DIN 53113). Changes in mechanical strength are given as folding endurance in tables I-IV.

Table I. Sample BIOTOP 3, permanent paper according to Austrian Standard A-1119. Reference, deacidified and artificially aged. Results of mechanical and chemical tests. ** ste = short term exposure—24 hours—in polluted atmosphere; SO₂ concentration 130 ppb, NO_x concentration 315 ppb, RH 65%.

Paper treatment	Folding endurance DIN 53412	pH DIN 53124	Alkaline reserve meq/kg
BIOTOP 3 untreated	20	9.2	2030
BIOTOP 3 FMC	12	10	2682
BIOTOP 3 FMC ste**	8	9.6	2366
BIOTOP 3 ÖNB	15	9.4	2200
BIOTOP 3 ÖNB ste	13	9.5	2140
BIOTOP 3 DEZ	11	9.2	2165
BIOTOP 3 DEZ ste	11	8.2	2133
BIOTOP 3 aged 32 days 80°C, 95% RH	8	8.8	ne

Table II. Sample FEDERLEICHT; classical book paper. Reference, deacidified and artificially aged. Results of mechanical and chemical tests.

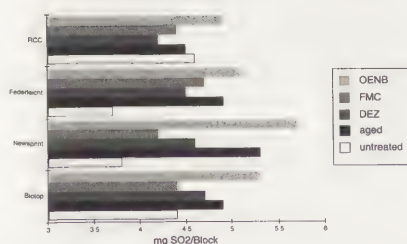
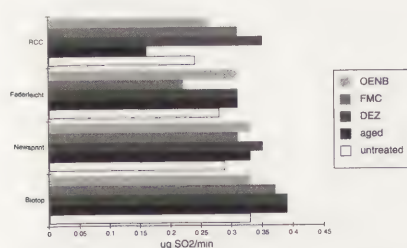
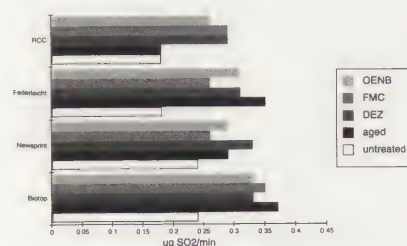
Paper treatment	Folding endurance DIN 53412	pH DIN 53124	Alkaline reserve meq/kg
FEDERLEICHT untreated	13	9.1	265
FEDERLEICHT FMC	8	9.1	433
FEDERLEICHT FMC ste	5	9.4	347
FEDERLEICHT ÖNB	6	9.3	312
FEDERLEICHT ÖNB ste	ne	9.0	248
FEDERLEICHT DEZ	9	8.9	408
FEDERLEICHT DEZ ste	8	8.1	384
FEDERLEICHT aged 32 days 80°C, 95% RH	4	8.5	ne

Table III. Sample RECYCONOMIC; recycling paper. Reference, deacidified and artificially aged. Results of mechanical and chemical tests.

Paper treatment	Folding endurance DIN 53412	pH DIN 53124	Alkaline reserve meq/kg
RECYCONOMIC untreated	4	5.4	—
RECYCONOMIC FMC	4	8.1	28
RECYCONOMIC FMC ste	3	7.9	23
RECYCONOMIC ÖNB	5	5.9	—
RECYCONOMIC ÖNB ste	4	5.6	—
RECYCONOMIC DEZ	3	7.7	136
RECYCONOMIC DEZ ste	3	7.7	139
RECYCONOMIC aged 32 days 80°C, 95% RH	0	4.6	—

Table IV. Sample Zeitungsrotationspapier; newsprint with alkaline filler and neutral sizing. Reference, deacidified and artificially aged. Results of mechanical and chemical tests.

Paper treatment	Folding endurance DIN 53412	pH DIN 53124	Alkaline reserve meq/kg
NEWSPRINT untreated	6	8.4	53
NEWSPRINT FMC	5	9.1	188
NEWSPRINT FMC ste	4	8.6	128
NEWSPRINT ÖNB	5	8.5	107
NEWSPRINT ÖNB ste	4	8.4	96
NEWSPRINT DEZ	5	8.7	301
NEWSPRINT DEZ ste	5	7.9	283
NEWSPRINT aged 32 days 80°C, 95% RH	4	6.8	—

Figure 3. Uptake of SO₂ (mg/min) by long-term exposure, exposure time 28 days.Figure 4a. Uptake of SO₂ (µg/min) by short-term exposure, exposure time 10 minutes.Figure 4b. Uptake of SO₂ (µg/min) by short-term exposure, exposure time 24 hours.

The alkaline reserve was determined according to the procedure described by Daniel, Flieger, and Leclerc (10). The pH was measured as cold extraction pH according to DIN 53124; in addition the sizing number was evaluated according to TGL 3024-56. Summarized data for pH and alkaline reserve is shown in tables I-IV. Measurement procedures for the determination of uptake of SO₂ and NO_x are described above (long-term and short-term exposures).

Concerning the SO₂ absorption, it can be stated that by the long-term exposure, the untreated papers showed generally lower absorption rates than the treated papers. An exception was evident with the RECYCONOMIC paper, in which the untreated sample had a higher absorption rate than the artificially aged paper, the DEZ-treated paper, and the paper deacidified after the FMC-process. The absorption rates of the other investigated papers (BIOTOP 3, FEDERLEICHT and ZEITUNGSROTATIONSPAPIER (NEWSPRINT)) did not differ much from each other. Samples which were not deacidified showed the lowest absorption rate, followed by the samples deacidified with the FMC process. The next highest absorption rate was shown by the samples deacidified with DEZ, and the highest rate of absorption was found in samples deacidified with the ÖNB-process. The results are summarized in Figure 3.

The uptake of SO₂ by short-term exposure showed similar trends. Here, too, the absorption rates of deacidified or artificially aged papers were altogether higher than the rates of untreated paper samples. This trend was particularly well pronounced at the end of the exposure time (24 hours), since the absorption rates of the untreated papers, compared to deacidified or aged papers, decreased considerably. The different paper types showed different rates of SO₂ uptake. Under the exposure conditions, the RECYCONOMIC paper had the lowest absorption rate, followed by FEDERLEICHT. The data of SO₂ uptake for the papers under investigation during short-term exposure are summarized in Figs. 4a and 4b.

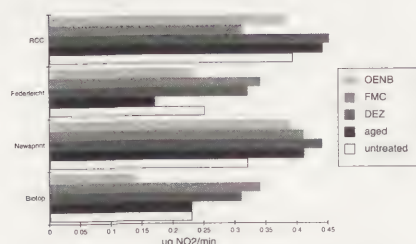


Figure 5a. Uptake of NO_x ($\mu\text{g}/\text{min}$) by short-term exposure, exposure time 10 minutes.

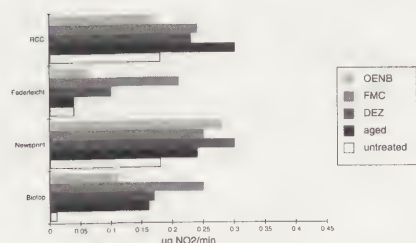


Figure 5b. Uptake of NO_x ($\mu\text{g}/\text{min}$) by short-term exposure, exposure time 24 hours.

The absorption of nitrogen oxides was not uniform for the different paper samples, although it can be stated that throughout short-term exposure artificially aged or deacidified papers revealed higher absorption rates. While at the beginning of exposure untreated papers had relatively high rates of absorption, their uptake of NO_x decreased considerably during the exposure time. The most pronounced effect in this regard is to be observed by BIOTOP 3, where the rate of absorption decreased from $0.23 \mu\text{g}/\text{min}$ to $0.01 \mu\text{g}/\text{min}$, and by the sample FEDERLEICHT where the uptake fell during exposure time from $0.28 \mu\text{g}/\text{min}$ to $0.05 \mu\text{g}/\text{min}$. Relatively high absorption rates can be observed by ground wood containing samples such as ZEITUNSPAPIER (NEWSPRINT) ($0.32 \mu\text{g}/\text{min}$ to $0.18 \mu\text{g}/\text{min}$) and RECYCONOMIC ($0.38 \mu\text{g}/\text{min}$ to $0.18 \mu\text{g}/\text{min}$). These findings were in good correlation to the recently published results of Lanting, in whose opinion the presence of lignin accounts for this effect (11). Summarized results are given in Figures 5a and 5b.

Conclusions

In relation to the behavior of paper exposed to atmospheric pollutants, the data of mechanical and chemical tests of untreated, deacidified, and artificially aged modern paper obtained thus far allows the following conclusions to be drawn. All deacidification under investigation caused a decrease in the mechanical strength of the treated papers both by folding endurance and by tensile strength; the data for tensile strength are not given in the tables. It is evident that deacidification by means of the FMC and the DEZ process led to an increase in the alkaline reserve of all paper samples, while the ÖNB technique in one case (RECYCONOMIC) failed to deposit an alkaline reserve in a measurable concentration.

A general trend was observed, in that the deacidification treatments investigated obviously promoted the absorption of acidic atmospheric pollutants, probably due to the presence of active reaction sites. The absorption rates were quite different and seemed to depend on the paper type. In addition, it was observed that uptake of SO_2 under exposure conditions took place primarily on paper sheets on the block surface, while the sheets from the center of the block showed no measurable sulfur content. Finally, it should be mentioned that according to the sizing number results, there is some evidence that the original size was removed (or made ineffective to a considerable extent) by liquid phase deacidification treatments by both the ÖNB process and the FMC-Lithco technique. It seems adequate that, besides the behavior of cellulose, other components of paper such as sizes should be considered in future research in order to form a clear judgement of the advantages and disadvantages of mass deacidification processes.

Acknowledgements

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Abstract

The aim of this work was to determine reasons why watercolour paintings are fugitive on aqueous washing. The solubility of gum arabic binder was identified for attention. Solubility of the gum arabic binder on paper substrates was studied. Artificial aging resulted in increasing insolubility. A commercially available watercolour paint also developed wash fastness on aging. A gum-pigment mixture has enhanced opportunities for the development of insolubility due to interactions between the gum and pigment. Although the paint studied developed wash fastness at 60°C, pure gum arabic did not decrease its solubility. Using partially non-aqueous solutions for washing reduced both the solubility of gum arabic and the fugitive nature of the paint.

Keywords

Watercolour, pigment, gum arabic, washing, solubility

The Effect of Gum Arabic Solubility on the Washing of Watercolours

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Introduction

The use of liquid treatments, often aqueous, are commonplace in paper and textile conservation. An unwanted side effect is the movement of pigment particles from one part of the surface to another or complete loss of pigment into the washing liquid. This paper reports some of the results obtained at the start of an extensive investigation into the effects of washing on paper and textiles, and concentrates on the development of insolubility of gum arabic binder in watercolour paints on paper.

Watercolour painting

The essentials of a watercolour painting are (i) that the paints are dispersible in water and (ii) that the paints are applied thinly so that the underlying paper still contributes to the eventual colour and texture of the painted area.

Although a usable paint could be made by merely mixing finely divided pigment into water, a binder and surfactant are usually incorporated. Gum arabic (acacia) is often used as a binder, but sugar, honey, dextrine and glue have also been used. After 1840, watercolour supplied as dried cakes often contained an ingredient such as glycerol to aid dispersion when rewetted (1). However, some cakes tend to be easier to disperse than others. Ox-gall is a traditional surfactant, but synthetic materials are now used.

Gum arabic

Gum arabic is a water-soluble polysaccharide consisting of a linear polymer of several sugars. The principal sugar is known as arabinic acid which is present both as the acid and as a salt with calcium, magnesium, and potassium cations.

Gum arabic is widely used in industry in pharmaceutical and other manufacturing methods as it is an excellent suspending agent for particles in aqueous solutions. It will prevent colloids being precipitated by ionic solutions (2).

The natural aging of gum arabic has not been studied, however, dry heat aging at 100–170°C has been investigated (3). When the aged gum was placed in water it was found that the amount of water absorbed by the gum decreased with an increase in aging temperature. One common reason for development of insolubility in polymers is crosslinking; extensive crosslinking leads to an increase in molecular weight and, therefore, to insolubility. However in this case, insolubility increase was attributed to irreversible loss of water from gum micelles, a physical rather than chemical change in the gum. Aging temperatures varied from 100 to 170°C. Complete insolubility was effected at 170°C. Time of aging was not stated.

Other evidence for the development of insolubility on aging comes from inspection of old gum arabic powder dissolved in cold water. In many cases, small particles of swollen gum, which persist for several days, can be seen in the water. Furthermore, old watercolour cakes are often more difficult to dissolve than the new ones, a phenomenon known as gelling. However, as this property depends on the pigment, it is likely that insolubility is brought about by an interaction between the pigment and the gum. Gum arabic can be precipitated from aqueous solutions by ethanol or ferric ions (4). Hence, the addition of alcohol to water may inhibit the solubility of gums when artifacts are washed.

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Mayer (5) gives a typical formulation for a vehicle for watercolour pigment as follows:

Gum arabic	2 ounce
Water	4 fluid ounce
Honey water, sugar syrup, or glucose	1¼ fluid ounce
Glycerine	1½ fluid ounce
Wetting agent	2-6 drops
o-phenyl phenol	¼ teaspoon

Paints may be used on many types of paper other than those specially prepared for use with watercolours. Typically, a paper is a mat of cellulose fibres, possibly with a mineral filler, but always sized to a certain extent. Until recent years, the size was almost always gelatine, often with the addition of aluminum sulphate (papermaker's alum) or aluminum potassium sulphate. The pigment/paper interface may be schematically represented (See fig. 1). In thick layers of pigment, the uppermost pigment particles are resting on other pigment particles. Hence the composition of the dried paint layer is essentially the same as that of paint from the block or tube. As the paint layer is applied more thinly, the amount of binder between each fibre and pigment particle becomes less since the binder will be spread over the paper fibres, whether or not there is pigment there. There is a limit to the quantity of binder which can be removed from the pigment particles before the coherency of the paint film is lost. Below the minimum pigment:binder ratio, dry pigment particles are left.

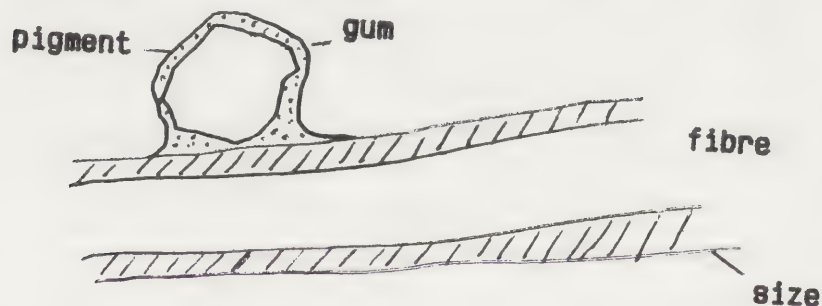


Figure 1. Schematic drawing of a pigment particle in a watercolour paint on paper.

Thus, on washing, the dispersibility of thickly applied paint can be predicted to be strongly influenced by the solubility of the binder while that of thinly applied paint depends additionally on the interaction of paint with the paper. In very thin paint where there is little binder, the fibre/size/pigment interactions are of most interest. If the size is removed from the fibres during washing, pigment may well be released from a painted paper. The general principles of detergency apply to pigments in the same way as they apply to dirt. Washing will be aided by surfactants and suspending agents. Although pigment particles have the advantage of being protected by a gum layer, if solubilised, the gum acts as a suspending agent and aids removal of the particles from the paper surface.

Effect of artificial aging on the solubility of gum arabic

One of the methods used for predicting the behaviour of materials is to artificially age them by placing them in an oven at an elevated temperature. In the experimental work described here, aging at 60°C and 100°C was used on gum arabic. So that the phenomenon could be studied easily, a 20% w/v solution of gum in distilled water was prepared and a layer of the solution was applied with a brush to one face of a weighed circle of filter paper (Whatman No 1). After 24 hours, the papers were reweighed. Solubility of the gum was determined by immersing the coated paper in distilled water for 60 minutes. The paper was then removed from the water and dried for 24 hours before reweighing. Ambient relative humidity averaged 50% and ranged between 40-55%. Weighings were performed on a balance capable of reading to 0.1 mg.

One of the effects of natural aging on paper is an increase in the oxidation of

paper due to absorption of air pollutants, such as oxides of nitrogen and sulphur, and by oxidation of cellulose. This results in a reduction in the pH of paper. The effect of pH on the aging of gum arabic was, therefore, studied. The pH of the 20% gum solution was measured using a combined glass electrode. The acidity of the gum was altered by adding a few drops of sulphuric acid to the gum and remeasuring the pH. The effects of aging of gum of various pHs on paper at 100°C was studied at pH 3.5 and 3.9 and at the natural pH of the gum, 4.4.

Cellulose is hygroscopic and also exhibits a hysteresis effect on washing and drying. It is, therefore, difficult to obtain accurate and reproducible weighings on paper without the use of careful climate control and knowledge of the recent environmental history of the samples. Thus, in the average laboratory there is a potential error which could be introduced when paper samples are weighed. This measurement error might have been decreased by the use of glass as a support for the gum film, but this was not practical as the dried film adhered poorly to the glass substrate; gum arabic is a poor film-forming polymer compared with gelatine. It was decided to perform the experiment on paper, as it was expected that the change in solubility would be significantly larger than the experimental error. Moreover, the use of paper as the substrate was a closer model to a watercolour painting.

Effect of artificial aging on watercolour applied to paper

The problem of loss of watercolour pigment from paper is generally accepted as a potential problem in the conservation of watercolour paintings, however, there is a great variability in the fugitive character of paints. For the purposes of these experiments, a paint highly fugitive to washing was desired. A watercolour box manufactured by Winsor and Newton was taken and trial washes of eleven different colours made on both 5% gelatine sized paper and unsized filter paper; all the paints contained gum arabic as the principal binder ingredient. The 5% gelatine sized paper was made by first soaking gelatine in distilled water for two hours then heating to 60°C until the gelatine was dissolved. The gelatine was then used hot and brushed onto filter paper laid on a glass sheet until the paper was saturated. Excess liquid was blotted off with paper towel and the filter paper allowed to dry for 24 hours.

Unexpectedly, after washing, none of the paints applied directly to filter paper changed their appearance and only two paints—Winsor emerald and azure cobalt—were visibly fugitive on sized paper. The other nine pigments used were alizarin carmine, cadmium scarlet, Winsor blue, Winsor green, indigo, raw sienna, burnt umber, raw amber, and sepia.

Winsor emerald was chosen as a suitable paint to study because it was fugitive to aqueous washing. The pigment consists of acrylamide yellow with chlorinated copper phthalocyanine and zinc oxide (6).

Preparation of a large sheet of pigmented paper was essential to the study of the various parameters involved. A sheet of Whatman's No. 1 filter paper was sized with 5% w/v gelatine solution. When dry, it was flattened by lightly spraying with water and pressing between blotting papers. A suspension of paint in water was spread evenly over the surface using a wire wound bar coater (7).

Samples of this paper were cut into rectangles approximately 10 × 30 mm. A set of samples was aged at 100°C and another at 60°C. After various periods of aging, the papers were washed by immersing them in water at 20°C for one hour with gentle rocking of the container at ½ and 1 hour to disperse released pigment. The samples were then dried and assessed visually and by measuring the reflectance spectrum in a Perkin Elmer 551S ultraviolet/visible spectrometer, fitted with an integrating sphere.

Effect of ethanol and surfactant on loss of pigment on washing

Samples of painted paper were washed in solutions of industrial methylated spirit (IMS) in water of strengths ranging from 1 to 50% v/v. The effects of water with a few drops of the non-ionic surfactant Synperonic N were also assessed.

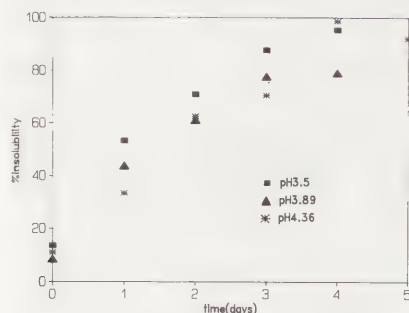


Figure 2. Development of insolubility of gum arabic on paper aged at 100°C.

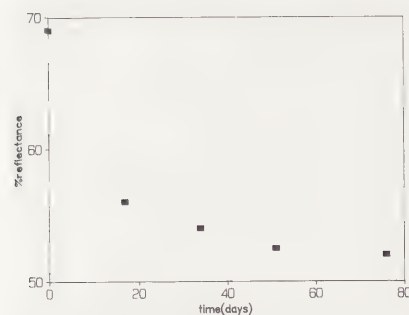


Figure 3. Reflectance of a watercolour wash after aqueous washing, aged at 60°C.

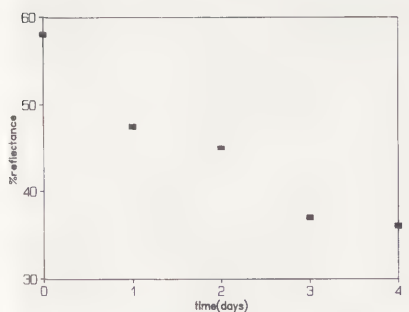


Figure 4. Reflectance of a watercolour wash after aqueous washing, aged at 100°C.

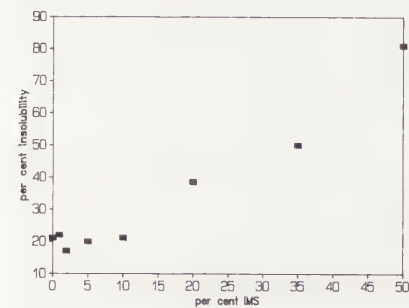


Figure 5. Development of insolubility of gum arabic on paper when increasing the ethanol concentration.

IMS was used in the experimental work instead of ethanol as a denatured form of ethanol would be used by conservators. IMS contains at least 95% ethanol, the balance being methanol and water.

Results

Effect of artificial aging on the solubility of gum arabic

Figure 2 shows the trend of results for aging at 100°C. It can be seen that the films became virtually insoluble after four days aging. There appears to be no trend in change of solubility with pH change. The change in solubility is large compared with the errors introduced by any lack of equilibrium of water content, thus justifying the experimental design.

At 60°, aging for periods of up to 100 days failed to produce a change in solubility over the experimental error, i.e., greater than 20%. A simple rule-of-thumb calculation on doubling the rate of reaction for a 10°C rise in temperature would predict the effects of aging to be clearly seen after 100 days of aging at 60°C if they are visible after one day at 100°C.

Effect of artificial aging on watercolour applied to paper

On aging at 60°C and 100°C, a distinct trend in decreased pigment loss is evinced by observing the samples. The trend is also illustrated in Figures 3 and 4, in which graphs are displayed of reflectance at 640 nm against aging time. The paper has a reflectance of 73.3% and the unwashed painted paper a reflectance of 35%.

Effect of ethanol on gum arabic solution

Figure 5 shows a loss of gum arabic solubility on increasing alcohol concentration (assuming ethanol is the causative agent in the industrial methylated spirit).

Effect of ethanol and surfactant on loss of pigment

Increasing the concentration of IMS in the wash water decreased the loss of pigment from the paper. Increasing the surfactant concentration to 0.047% increased the loss of pigment (See fig. 6). The reflectance measurements for addition of surfactant were 60% for 0.2% surfactant and 62.5% for 0.04% surfactant; pure water gave 50% reflectance. These results may be compared with the results for those shown in Figure 6, as these samples were washed at the same time. This illustrates that surfactant aids the loss of pigment on washing.

Discussion

Insolubility of pure gum arabic can be brought about by heating at 100°C and 170°C, but apparently not 60°C. This apparent failure of the Arrhenius equation casts doubt on the ability of gum arabic to become insoluble at room temperature. Gelling or hardening of paint cakes on aging is a problem for the watercolour manufacturer. As there is a wide variability in this effect with the pigment used, the interaction of pigment and gum on the development of insolubility is evidently important. A water fugitive paint, Winsor and Newton's Emerald green, was chosen for artificial aging at 60°C and 100°C. It became more stable to washing after being aged at both temperatures. Conservators believe old watercolours to be more stable to washing than new ones. An increase in insolubility of the gum could explain the decreased stability. The experimental work will be extended to include the effects of accelerated aging on other commercially available paints. However, preliminary work on several other paints aged at 100°C for three days indicates that wash fastness will increase.

Gum arabic can be precipitated from solution by ethanol. It was found that addition of ethanol (industrial methylated spirit) to the wash water decreased the loss of pigment considerably. Such an approach could be used if a conservator is washing water fugitive watercolour paints, however, ethanol soluble pigments, such as gamboge, would have to be absent.

A series of samples have been prepared for dark aging in ambient conditions.

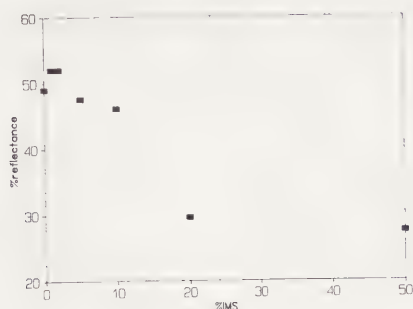


Figure 6. Reflectance of a watercolour wash after washing in ethanol/water.

Conclusions

The solubility of gum arabic binder is an important factor in the loss of paint from watercolours during washing. Artificial aging at 60°C and 100°C produces a reduction in the loss of a watercolour paint from paper. Aging at 100°C produces loss of solubility of pure gum arabic on a paper substrate, but aging at 60°C does not produce any detectable change. The principal mechanism for development of insolubility of gum arabic appears to be irreversible dehydration. However, in paints there appears to be an additional effect due to pigment-gum interaction. The reputed enhanced stability of old watercolours compared with new ones could be due to greater insolubility of the binder when aged.

One method for reducing the loss of paint from paper is to wash in alcoholic solutions. This method could not be used with alcohol soluble pigments, such as gamboge. The presence of ethanol in wash water will also change the solubility of stains.

Acknowledgements

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Materials

Whatman filter paper, gum arabic, Synperonic N: Merck Ltd., Leicestershire LE17 4XN, United Kingdom

Pigments and Paint: Winsor and Newton, Wealdstone, Harrow, Middlesex HA3 5RM, United Kingdom

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Abstract

Equipment for mechanized document restoration by filling missing parts of document leaves with paper pulp is discussed. The restoration process includes paper pulp preparation, leaf placement on the wire, casting process, and preliminary and final drying. All operations are combined in an integral working cycle on endless wire. A supercalender is used for paper finishing. To prevent penetration of transitional metal ions into the paper, water purification is necessary.

Keywords

Endless wire, filling of missing parts, leaf-casting system, mechanized restoration, paper dryness, paper pulp



Figure 1. The leaf-casting system.

Mechanized Document Restoration by Paper Pulp Filling Process

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Introduction

The idea of mechanized document restoration with paper pulp originated in the Document Conservation Department of the National Library of Russia in St. Petersburg in the 1950s. In 1969, a leaf-casting system was used in the department. The technological cycle of the complex plant involved a number of steps: preparation of paper pulp, preparation of a restored document by floating it in warm water (50–60°C), placing the paper on the casting form wire, and finally, completion of the casting process proper (pressing, drying, and paper finishing). For quite a number of years, by using this system, we restored multiple documents from the foreign collection of the library. Other materials, including manuscripts and those with evidence of biological deterioration, have also been restored.

The leaf-casting system has served as an adequate base for research and for the design of a next-generation item of restoration equipment. The new pattern differs from the previous one mainly in the absence of a pressing section, introducing a preliminary drying stage in the course of restoration; this allows for further dehydration and first-stage drying of the restored unit. Additionally, leaf spreading, casting, and drying have been integrated in a single technological cycle performed on an endless wire (See fig. 1).

The whole system, with equipment conventionally classified as basic and accessory, is located on two levels: the accessory equipment is placed one story lower. In the course of its operation, the restoration machine uses a considerable amount of water, which is generally known to be the main source of ions of transitional metals (for example, iron and copper). To prevent penetration of metals—catalysts of oxidation destruction of paper—into a restored unit, the technological cycle involves both mechanical and chemical water purification. For this purpose the water supply system is equipped with a filter filled with phosphate-cellulose ionite fibre, to absorb iron and copper ions from the water. After examination, it was found that the sorbent in sodium-hydrogen form with the substitution degree to Na from 45 to 80% benefits transition metal ion sorption, enriching the water with Na ions, decreasing paper acidity, and increasing its stability during storage (1). For the same purpose, all connections and tanks in the technological line are made of stainless steel.

The new leaf-casting system is operated at a significantly increased speed of fibre-pulp dehydration in the casting area. For additional water removal, a vacuum suction box is placed next to the casting area. For the purposes of paper finishing, the restoration machine is fitted with a double-roll calender, ensuring paper density, equal thickness of original document paper and new paper just cast in the place of missing parts and smoothing over wire marks.

The whole of the equipment can be divided into functional sections according to the following processes: paper pulp preparation process, material preparation and filling of missing parts, preliminary drying, final drying, paper finishing, and materials used in the restoration process.

Paper pulp preparation process

Preliminary examinations indicated that one of the principal problems of mechanized restoration—the forming of a strong joint between the old and the new parts—will be relieved to a considerable extent by using paper pulp of the following composition: cotton cellulose with the Schopper-Riegler freeness value of 45°, 5% thermohydroplastic vinol fibres as a binding agent, and 10% chalk as a filler for the cellulose pulp (2). The required separation freeness of cellulose fibres is attained by beating 1% concentration cotton cellulose for 35 minutes.

When the beating is completed, binder and filler are introduced into the roll, with mixing. Then the fibre pulp is poured into the intermediate tank and, at the air pressure of 1.5 atmospheres, squeezed out into the pulp mixer. There the pulp is diluted with water to 0.5% concentration. Further on, in the course of restoration, the amount of pulp required for casting is measured with a measuring tank to enter the second mixer where water is added to 140 litres.

Material preparation and filling of missing parts

Adequate quality of the joint between the old and new paper parts requires appropriate document treatment. With this in mind, the document is placed in a preparation tray filled with heated water. The temperature of 50–60°C is held automatically. In this way, the paper is decontaminated and cellulose fibres swell, permitting the development of inter-fibre bonds.

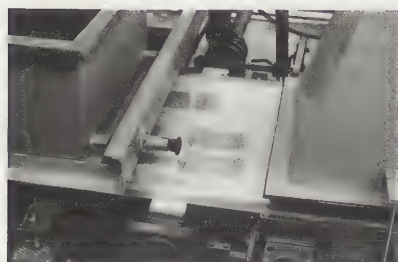


Figure 2. The vacuum suction box.

After removal from preparation tray the paper is placed on the wire in the spreading area, where the water level in the underwire bath permits permanent wire wetting. At this stage additional mechanical treatment of documents can be performed for complete decontamination, also benefitting the development of bonds with newly-cast paper parts (See fig. 2).

All of the following processes are centrally controlled. By pressing the button at the control panel the wire with restored material moves one step forward to the casting area. Then, in consecutive order, the casting form and the fixing device for retaining the leaves on the wire during fibre pulp delivery are lowered. At the next stage, the casting form is filled with water, supplied from under the wire, to 50–100 mm over its surface. The water layer prevents bubbling under the wire, ensuring uniform pulp distribution over the wire, where it is not covered by the paper. Then the pulp pump is operated to pump the fibre suspension from the second mixer to the casting form.

The process of casting starts when the first vacuum pump is switched on, and two seconds after the fixing device is lifted. The fibrous pulp then fills the missing parts of the leaf due to the high water filtration speed in the wire area vacant of paper. The dryness of newly-cast paper parts after casting is 15%.

To move the restored unit to the next area, the wire drive is activated, with simultaneous automatic lifting of the casting form, fixing device and the hood over the preliminary drying area, further along the line. Moving from the casting area to the preliminary drying area the unit passes over the vacuum suction box; this increases the dryness of newly-cast paper parts to 20%.

Preliminary drying

The previous leaf-casting system pattern involved pressing of the resulting unit in a flat cloth press for further dehumidification. In doing this, uniform humidity was attained in the restored document and in the newly-cast part. The pressing process lasted for 7–8 days.

It is generally known that in papermaking the paper arrives to the drying section at 45% dryness (3). The current restoration machine design contains a preliminary drying area, consisting of a heater, fitted into the upper part of the drying hood, and a vacuum box with a perforated upper plate. In a working position, the rubber cushion of the drying hood is supported on the perforated plate on hinges. When the second vacuum pump is activated, air heated to 200°C by the air heater is blown through the paper. The angle of taper (conicity) of the hood and the velocity of air flow ensure adequate unit dryness at the paper surface temperature of 55–60°C.

The restored material has a tight structure that was developed in the process of papermaking. It seems natural, therefore, that it demonstrates higher resistance to the air flow than the porous newly-cast parts, where hot air penetrates easily and drying is thus more intensive. Simultaneously, the difference in dryness between the original and the newly-cast parts of the documents decreases, so that the unit leaves the preliminary drying area with the old paper dryness of 50%, and the new one of 59%. The stage of preliminary drying begins with

the development of bonds in a paper leaf, as with an increase in dryness from 35 to 60% there is capillary dehumidifying and inter-fibre shrinkage (4).

Due to a special design feature, resulting from a special arrangement of drying cylinders, at the next stage the restored unit is at rest. Only at the next wire step does it move to the area of final drying.

Final drying

The drying section of the equipment consists of two chrome-plated cylinders, with one of them electrically heated. The temperature is held automatically at the level of 85–90°C. To reduce mechanical effects on the paper and probable joint damages the restored unit is placed on the upper cylinder so that its surface touches the wire. The temperature of the paper surface is 75–78°C and is bound up with the presence of vinol fibres in the paper composition. The time of drying is 2–3 minutes. At this temperature and at the retained humidity the vinol dissolution takes place, and the additive bonds are developed by hydroxyl groups of vinol and cellulose. Numerous former investigations have proved that vinol imparts strength, ageing resistance, durability to paper, so, the different temperature conditions are not reviewed in this report. The resulting leaves indicate dryness of 94–95%. With the wire moving one step forward, the restored material is transported to the lower cylinder, so as to be placed between the wire and the cylinder surface. The paper is then cooled and dehumidified to 1–2%, thus becoming more plastic. Additionally, static electricity is relieved from the material on the non-heated cylinder (See fig. 3).

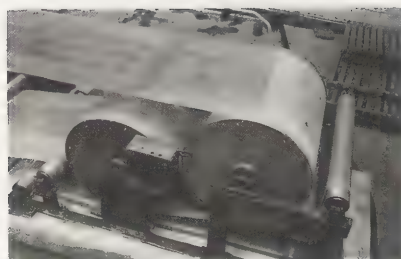


Figure 3. The final drying.

Paper finishing

For the purpose of finishing, a supercalender is used. It consists of two rolls: the upper roll is permanent and made of metal; the lower roll is renewable. There are three renewal versions: metal, asbestos-packed, and wool-packed. Pressure between the calendar rolls can be altered within the limits of 0.1 to 0.5 MPa, and the upper roll temperature can range between 20–120°C. Gloss rate, transparency, density, and other paper properties depend on the renewable roll version. Our investigations indicated a superior paper finishing quality was achieved with the obtained asbestos roll (2).

Materials used in the restoration process

The paper pulp was intended for use in the mechanized restoration by the paper pulp filling process. The following materials were used: cotton cellulose (viscosity of 1% solution was 301–410 mPa·c); the water-soluble, thermoplastic fibre vinol, (fibre length 5 mm, fibre thickness 176 tex); and calcium carbonate (chalk) that had been cleaned and recrystallized twice.

Conclusion

In conclusion, the authors would like to note that major contributions to the development of the previous leaf-casting systems have been made by Dr. M. Blank and Dr. J. Nyuksha.

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Résumé

Les oeuvres d'art peuvent souffrir lors du déménagement d'un musée mais cela peut aussi leur être bénéfique car c'est un moyen de revoir la totalité d'une collection et d'en contrôler l'état. C'est à cette occasion que le travail sur les éventails du musée Carnavalet a été entrepris. Cet article nous montre les diverses solutions adoptées pour un rangement simple et une manipulation aisée, ainsi que la remise en état des éventails les plus endommagés. Après un bref historique, une description des différents traitements est exposée—le gommage, le décollage, le renfort, le comblage des lacunes, le replissage—avec, en exemple, trois cas particuliers.

Mots clefs

Conservation préventive, matériaux composites, gel de synthèse, thermocollage, replissage, éventails, restauration

Conservation d'une collection d'un millier d'éventails au musée Carnavalet

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Introduction

Le musée Carnavalet, spécialisé dans l'histoire de Paris, conserve des collections d'une très grande variété: mobilier, numismatique, peintures, sculptures, dessins, gravures, photographies et objets d'art. Entre autres, une collection d'éventails plus documentaires que prestigieux, hormis quelques uns dont: un éventail ayant appartenu à l'impératrice Eugénie, quelques beaux éventails du XVIII^e siècle, «le jour et la nuit», dessiné par Maurice Leloir, «le siècle finissant, le siècle commençant» par Maurice Leloir et exécuté par Duvelloy.

Cette collection en grande partie constituée par le legs de Madame Francisque, en 1907, est d'une grande diversité. Les thèmes principaux en sont la période révolutionnaire et la publicité.

Excepté quelques éventails exposés dans les salles, la majeure partie était conservée dans une réserve très mal climatisée, dans le grenier du musée. Faute de place, ils étaient serrés dans des tiroirs et protégés de la poussière dans des poches en plastique.

A l'occasion de l'agrandissement du musée, en 1989, pour le bicentenaire de la Révolution, un récolement complet de la collection a été effectué. Nous avons appliqué à l'éventail nos connaissances de spécialistes de la restauration des oeuvres graphiques.

Contrairement aux dessins et aux gravures, l'éventail est un document en trois dimensions composé de matériaux très divers. Dans la mesure du possible, il doit garder ses fonctions premières: s'ouvrir et se fermer à volonté.

C'est un objet utilitaire et de frivolité qui n'a jamais été conçu pour durer, ce qui explique sa grande fragilité.

Historique

A l'origine, les éventails sont fixes et munis d'un long manche. En Egypte, ils servent à éventer le pharaon et à chasser les insectes. Chez les Grecs, ils sont toujours fixes mais le manche est plus court pour un usage moins cérémonieux. A ses débuts, l'église chrétienne adopte l'usage du «flabellum». Petit à petit il est supprimé de la liturgie romaine sauf pour le service solennel du souverain pontife jusqu'à Vatican II où il disparaît complètement.

Il apparaît en France dès le XIV^e siècle pour les dames de la cour. C'est «l'es-mouchoir» qui deviendra «l'esventoir» pour arriver enfin à «l'éventail».

Au XVI^e siècle, nous trouvons déjà les différents types d'éventails:

- les éventails pliés (avec feuilles) ou brisés (sans feuille),
- les éventails en touffe de plumes montés sur un manche,
- les éventails en drapeaux,
- les éventails cocardes.

Au XVII^e siècle, l'éventail gagne toute l'Europe et pénètre dans toutes les couches de la société. Paris devient alors un grand centre de fabrication. L'éventail est peint sur canepin (fleur de cuir destinée à recevoir une peinture pour faire la feuille) et sur taffetas.

Au XVIII^e siècle, on le porte à toute heure, en toute saison et il est accessible à toutes les bourses. Il devient aussi objet de badinage et comporte un langage. Une académie à Londres, citée par Addison, enseigne la manière d'en jouer: exercice en six temps «Prenez vos éventails, déferlez, déchargez, mettez bas,

agitez, fermez vos éventails». Il existe les éventails galants et de mariage, mais nombreux aussi sont ceux qui traitent de l'actualité, particulièrement la période révolutionnaire avec des commentaires sur les principaux événements. En 1780, les éventails sont imprimés et rehaussés de gouache (influence anglaise). Sous Louis XVI, de nombreux éventails sont peints sur soie, pailletés, brodés, ornés de marqueterie. Il y a aussi les éventails à surprises: celui du jeu «vu sans être vu», celui de la lorgnette, où une petite loupe est cachée dans la rivure, ou encore celui des jeux à la mode tels que devinette et loterie.

Après la Révolution, la noblesse, clientèle privilégiée des éventailistes, est ruinée ou émigrée. Sous l'Empire, la mode change. Les robes deviennent légères et sans poche, les femmes portent le petit sac appelé «réticule» où se glissent le mouchoir et l'éventail. Ses dimensions se réduisent et l'éventail prend le nom de «lilliputien» ou «d'imperceptible».

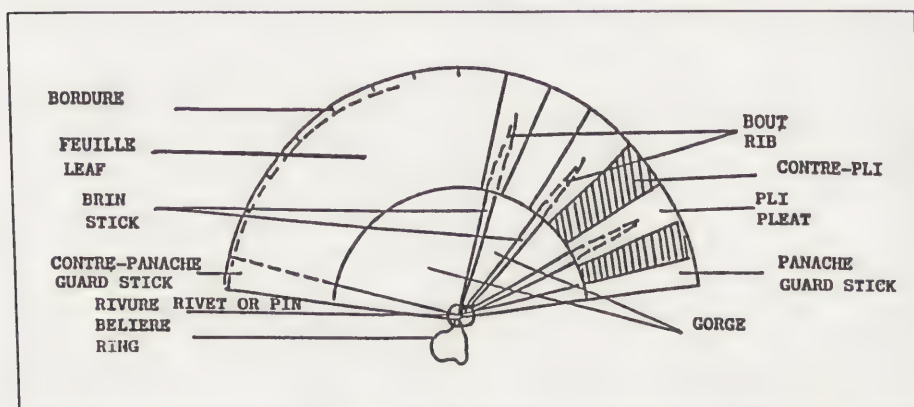
Les décors figuratifs disparaissent peu à peu et sont remplacés par des motifs géométriques et d'arabesques faits de paillettes. La mode et la politique ne favorisent pas le développement de l'éventail. Il n'y a plus d'exportation.

Sous la Restauration, la duchesse du Berry remet l'éventail à la mode et la bourgeoisie riche, qui devient la classe dirigeante du pays, s'y intéresse. L'invention de la lithographie et de la chromolithographie vont permettre une grande diffusion, et le commerce de la copie des styles des XVII^e et XVIII^e siècles va devenir florissant. Les fabricants d'éventails modernisent leur outillage et profitent des progrès techniques du XIX^e siècle. Les éventails de publicité vantant les nouveaux produits, spectacles, restaurants ainsi que l'éventail souvenir—gala, bal, exposition universelle—apparaissent un peu avant la Belle Epoque, période faste pour l'éventail.

Anonymes sous l'Ancien Régime, les beaux éventails sont, au XIX^e siècle, très souvent signés par les fabricants tels que Duvelleroy, Alexandre ou Kees. Les ivoiriers de Dieppe et de Méru réalisent les montures. Les feuilles sont souvent signées par de grands artistes comme Gavarni, Rosa Bonheur, Louis et Maurice Leloir, Forain, Redon, Louise Abbema, et Corot.

Descriptif

Un éventail se compose de deux parties: la monture et la feuille (voir figure 1).



1. La monture, partie inférieure et rigide de l'éventail peut être en bois, corne, os, écaille ou ivoire. Elle est constituée de:
 - la gorge: ensemble de brins terminés par les bouts (ou flèches) qui portent la feuille.
 - des maîtres-brins qui protègent l'éventail fermé, appelés le «panache» (dessus) et le «contre-panache» (dessous).
 - la rivure, fixée à la tête de l'éventail, réunit les brins et les panaches à leur base. Un anneau (bêlière) qui peut être maintenu à la rivure permettant de passer une dragonne ou une chaînette pour suspendre l'éventail au poignet.

2. La feuille, partie supérieure de l'éventail, est portée par les bouts et souvent doublée d'une contre feuille. Les matières employées sont le papier, la peau, la soie, le satin, la dentelle, le tulle et la plume. Les éventails sont dits pliés ou brisés.
 - les pliés sont constitués d'une monture et d'une feuille plissée. Le pli est la partie de la feuille plissée sur laquelle est collé le bout et s'oppose au contrepli qui est libre.
 - les brisés sont constitués de lamelles reliées entre-elles par un ruban coupé et sont sans feuille.

Conservation

Tous les éventails de la collection ont été reclassés par ordre de numéro d'inventaire. Ceux qui étaient particulièrement endommagés ont été répertoriés et photographiés pour une restauration ultérieure. Ils ont tous été dépoussiérés avec de petites brosses fines; les montures ont été nettoyées et les rivets ôtés quand cela était possible. Les montures de bois ont été légèrement frottées avec des tampons imprégnés d'essence de térébenthine et les bois blancs simples gommés. Celles en ivoire ont été nettoyées avec des tampons imprégnés de savon à la glycérine et rincées. Sur la nacre et l'écaille on a passé une poudre tripoli de Venise [1] mélangée à de l'eau et de l'alcool. La solution spéciale argenterie de la maison Puiforcat [2] a redonné de l'éclat aux incrustations d'argent.

Des boîtes ont été confectionnées dans un carton neutre stratifié gris et blanc, solide à la lumière, d'une épaisseur de 650 afa: le Folding Box board [3]. Quatre formats ont été retenus et chaque éventail est conservé fermé dans sa boîte. Certains, particulièrement fragiles, sont conservés, ouvert à plat, dans des boîtes confectionnées avec le même matériau. Les boîtes d'origine des éventails, peu nombreuses, sont conservées à part, ce qui permet de ranger toute la collection par ordre de numéro d'inventaire par rapport aux formats dans un même ensemble de boîtes. Certains sont exposés en alternance, dans les salles permanentes du musée, particulièrement dans les salles de la Révolution.

Altérations

Les montures les plus abîmées sont celles de nacre, d'ivoire ou d'écaille très travaillées, sculptées et repercées. Les montures de bois sont peu endommagées. Les panaches ainsi que les bouts sont très souvent cassés au niveau de la feuille et de la monture.

La feuille est la partie la plus fragile. Les éventails sont souvent restés dans le fond d'une armoire ou d'un tiroir, sans soin particulier et, au fil des années, les soies et les papiers se sont jaunis et flétris. Le fait d'ouvrir et de fermer constamment l'objet a affaibli considérablement les pliures. Les soies, très fines, s'effilochent. La peau et les papiers se cassent. Les décors s'altèrent. Les panaches sont souvent séparés du corps de l'éventail. Plis et contre-plis ont parfois entièrement disparu. La diversité des matériaux—peau et papier par exemple—amène des différences de tension qui endommagent la couche picturale. Des anciennes réparations ont été faites avec un papier calque fort qui rend la fermeture des éventails très difficile. De nombreuses lacunes laissent apparaître les bouts et fragilisent encore davantage l'éventail.

Restauration

Les montures nettoyées, notre travail consiste à remettre les feuilles de papier ou de soie en état.

Le gommage est la première opération à envisager. La gomme électrique est très utilisée car elle est très douce et permet de gommer de petites surfaces en évitant les décors, les paillettes, les broderies.

Il faut ensuite éliminer toutes les «réparations» ajoutées antérieurement pour consolider l'éventail. Cela peut être du papier vergé ou cristal, de la peau sciée, des cartonnages, du papier calque ou de la mousseline, collés avec des adhésifs divers. De nombreuses pertes ont été certainement évitées grâce à ces renforts

qui n'ont cependant pas toujours été posés dans les meilleures conditions de conservation. Pour les supprimer, différentes méthodes de décollage ont été envisagées:

La chambre à humidification semblait idéale car elle permet d'obtenir un travail en profondeur sans trop d'humidification, mais cette méthode est impossible à appliquer à cause des montures qui risquent de se déformer. Par ailleurs, l'emploi du Gore-tex [3] (membrane de téflon laminé sur un feutre de polyester), appliqué localement permet un contrôle du passage de l'humidité, mais risque également de faire réagir les bouts de la monture à l'intérieur des deux feuilles.

Finalement, nous avons adopté quatre méthodes:

- Le décollage mécanique: surtout utilisé pour retirer certains calques qui doublaient en plein la contre-feuille.
- Le décollage à la vapeur employé particulièrement pour les papiers et la colle forte. Cette méthode est à éviter lorsque les feuilles sont en peau, celles-ci se rétractant à la chaleur. Il est bien évident que les décors sont également à surveiller et ce type de décollage n'est pas recommandé pour les gouaches.
- La spatule chauffante, combinée avec un buvard humide, permet un décollage très localisé des renforts et le dédoubleage de la feuille et de la contre-feuille.
- Le gel de synthèse [4] (silicate de sodium, de magnésium et de lithium) a été utilisé pour la majeure partie des décollages. Il apporte un minimum d'humidité et permet de par sa nature basique, d'éliminer en partie les jaunissements dus aux adhésifs.

Lorsque tous les renforts sont retirés, l'éventail est bien souvent dans un triste état: les panaches sont séparés du corps de l'éventail; la majorité des pliures sont cassées et de nombreuses lacunes apparaissent. Il s'agit alors de reformer l'éventail en rattachant plis et contre-plis le plus discrètement possible mais avec solidité.

Quand la feuille est doublée, il est souhaitable de glisser des renforts par l'intérieur, mais parfois les matériaux employés sont si fragiles qu'il est impossible de les séparer. La restauration s'effectue alors au dos de la contre-feuille. Cette méthode est également valable pour les éventails dits «montés à l'anglaise» où la feuille, sans doublure, laisse les bouts apparents.

Nous avons choisi deux méthodes de renfort:

L'une, par thermocollage, consiste à couper des bandes de 5 millimètres de largeur dans un rouleau de *Heat-set repair tissue* [5] (papier très fin à fibres longues collé sur un adhésif acrylique à ph neutre): ces bandes sont appliquées au dos de l'éventail entre deux téflons avec une spatule chauffante (environ 850°C).

Cette méthode a deux avantages: la rapidité d'exécution, et l'absence d'humidité qui résout les problèmes de séchage.

L'autre méthode consiste à renforcer les pliures avec des bandes de papier Japon *Kuzo* de chez *Paper Nao* [3]. Dans ce cas, on a le choix du papier, de la coupe et de l'adhésif. Le papier est choisi en fonction de sa couleur et de sa transparence, le grammage peut aller de 5 g/m² à 33 g/m². Ces bandes de papier sont coupées en biais pour suivre le sens de la feuille de l'éventail et humidifiées pour éviter la coupe franche et conserver les fibres du papier. Les adhésifs sont choisis en fonction du résultat recherché:

- La colle d'amidon de blé *Zin Shofu* [3], adhésif puissant, est employée pour les papiers forts, les toiles et pour raccorder les maîtres brins au corps de l'éventail.
- La *methylcellulose tylose MH 300* [4,5] est préférée pour les papiers très fins, décorés au revers et pour le doublage. Cet adhésif est très souple et garde une bonne transparence.
- L'hydroxypropylcellulose *Klucel G* [4,5] est très appréciée lorsque plusieurs matériaux sont en présence: peau de cygne et papier par exemple. Cet adhésif étant employé en milieu alcoolique, évite l'humidité et permet le choix du papier Japon.

Il peut être intéressant de combiner les deux méthodes de renfort: par exemple, lorsque les pliures sont séparées, le papier roule et se recroqueville. Des petits

ponts de quelques millimètres peuvent être posés par thermocollage pour maintenir les bords de la feuille à l'intérieur et une bande de Japon est alors collée sur la totalité de la pliure.

L'éventail étant maintenant restauré, il faut le replisser avant de le fermer et de le ranger dans sa boîte. Chaque pliure est façonnée sur une forme faite de deux morceaux de cartons en forme de toit; le pliage se fait alternativement sur la face et sur le dos pour obtenir le pliage «accordéon». Un «non tissé» est posé sur la feuille au moment du façonnage pour protéger le décor.

Application de ces méthodes de restauration à travers trois exemples:

1° Apparition et conseils de Henri IV à Louis XVI ou la vérité découverte

XVIII^e siècle populaire. Inv. Ev. 119

Face: gravure coloriée sur papier vergé avec une grande scène centrale; chanson à droite et à gauche dans des cartouches

Revers: papier vergé non historié

Monture: bois foncé, 12 brins—Ht. 28,5 cm; Hf. 13,5 cm

Pour éviter le démontage complet de cet éventail, qui était en très mauvais état, la feuille du dos a été en partie retirée afin d'intervenir au verso de la face de la feuille.

De nombreuses restaurations anciennes avaient été effectuées au verso et à l'intérieur des feuilles avec du papier cartonné et de la colle forte.

Le décollage de la contre-feuille a été effectué à la vapeur et la colle forte éliminée par la chaleur. Il était beaucoup plus aisé d'intervenir au verso de la feuille après avoir soulevé en partie la contre-feuille. Les lacunes de la face ont été comblées avec du papier vergé de même nature que la feuille tout en respectant les vergeures et les pontuseaux. Des bandes de papier Japon ont reconstitué les pliures. Les parties de la contre-feuille soulevées ont été doublées avec un Japon 5 g/m² à la méthylcellulose et refixées les unes aux autres après avoir laissé dépasser le papier Japon de 5 millimètres des parties doublées.

Les panaches ont été également refixées à la feuille par le même procédé après soulèvement du papier collé sur les maîtres brins. L'éventail a été ensuite replissé.

2° Planche d'assignats

XVIII^e siècle. Directoire. Inv. Ev. 164

Face: eau forte noire et sepia sur papier vergé

Revers: papier vergé non historié

Monture: palissandre et ivoire, 18 brins—Ht. 24,4 cm; HF. 16 cm

Le panache était séparé du corps de l'éventail. Le papier de la feuille, très abîmé, avait été renforcé avec des morceaux de papier appartenant à d'autres «planches d'assignats». Les bouts étaient presque tous cassés à 1 cm de la gorge à l'intérieur des feuilles et la contre-feuille très lacunaire. La rivure était constituée d'un clou rouillé, aplati de chaque côté.

Le début du décollage de la contre-feuille a été effectué sans démonter le rivet rouillé, mais étant donné l'état de cet éventail, il fallait l'ôter. Avec une micro-perceuse, le clou a finalement été dégagé en l'usant progressivement.

Les différents morceaux de la contre-feuille qui restaient sur l'éventail ont été décollés à la vapeur. Ils ont été doublés, avant le comblage des lacunes, sur la table à vide avec un Japon Kuzo 5 g/m² à la méthylcellulose. Les manques—2 plis, 2 contre-plis et le pli correspondant au contre-panache—ont été remplacés par un papier vergé de même nature, teinté dans une décoction de grains naturels (chicorée) et collé sur le papier Japon de doublage.

Les brins qui étaient cassés, se sont séparés des bouts, après le décollage de la contre-feuille. Chaque brin a été refixé à son bout avec des petits morceaux de carton neutre élagués aux extrémités et collés avec un acétate de polyvinyle neutre *Syntha A 2240* de chez HENKEL [5].

Les plis et contre-plis ont été rattachés ensemble avec des bandes de papier Japon,

la feuille et la contre-feuille réajustées ensemble et les panaches refixés. La bordure, faite d'une bande de Japon coupée en biais et pliée en deux pour être posée à cheval sur les feuilles a été fixée à la colle d'amidon. L'éventail a été ensuite replissé.

3° Restaurant espagnol, 4 rue du Helder, Paris

Face: feuille imprimée en couleur

Revers: feuille imprimée, lettres noires

Monture: bois blanc simple, sur le panache et le contre-panache est inscrit en lettres dorées "Restaurant Espagnol". 18 brins—Ht. 22 cm; Hf. 11,2 cm

Rivure: clou

Ce dernier exemple est un éventail de publicité non inventorié, entièrement détérioré par les vers.

Dans ce cas il fallait démonter entièrement l'éventail et séparer la feuille de la contre-feuille.

Le gel de synthèse et le jet de vapeur ont été utilisés pour le décollage. Après séparation des feuilles, le comblage des lacunes a été effectué sur une table à vide à la pulpe de papier. Pour faire cette pulpe, nous avons recherché un papier semblable à celui des feuilles de l'éventail et nous l'avons réduit en pâte à papier.

Pour retrouver une «mise au ton» exacte, chaque trou a été teinté au fur et à mesure du comblage avec de la gouache en poudre Winsor et Newton [6] mélangée à de la méthylcellulose et de l'eau.

Le comblage de la contre-feuille a été commencé en gardant les brins fixés sur le papier. Avec l'humidité ils se sont détachés les uns après les autres. Finalement tous ont été retirés.

Les deux feuilles ont ensuite été doublées avec un voile de papier Japon, à la méthylcellulose. Un replissage a été amorcé avant le remontage définitif. Chaque brin a été refixé sur les plis et la feuille a été réajustée à la contre-feuille. Elles ont été maintenues en haut et en bas par collage de 5 mm de largeur. L'éventail a été ensuite replissé définitivement.

Conclusion

La complexité de la restauration des éventails réside dans la diversité des matériaux qui sont utilisés.

Nous nous sommes efforcés de trouver des méthodes simples et rapides, mais chaque cas est particulier. A ce jour, quelques éventails seulement ont fait l'objet d'une restauration.

Etant donné l'ampleur de cette collection, Roselyne Hurel, le conservateur responsable du département des objets d'art a mis l'accent sur la conservation préventive. Chaque éventail est actuellement rangé dans de bonnes conditions, en attendant, pour certains, la restauration.

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Matériaux

- [1] Le tripoli: roche siliceuse friable originaire de la ville de Tripoli de Syrie (Liban). Le *tripoli de Venise* improprement nommé vient de l'île de Corfou. Société PMSB: 10, rue Saint-Bernard, 75011 Paris, France, tél. (1) 43 71 82 85

- [2] Puiforcat S.A.: 2 avenue Matignon, 75008 Paris, France, tél. (1) 45 63 10 10
- [3] Atlantis France: 2, rue des Petits-Champs, 75002 Paris, France, tél. (1) 42 96 53 85
- [4] Art et Conservation: 33, avenue de Trudaine, 75009 Paris, France, tél. (1) 48 74 95 82
- [5] STOULS: Z.A. des Godets—Rue des Petits-Ruisseaux, 91370 Verrière-les-Buissons, France, tél. (1) 69 20 44 35
- [6] LAVRUT: 52-56, passage de Choiseul, 75002 Paris, France, tél. (1) 42 96 95 54

Abstract

This project highlights the conservation of a paper dress manufactured by Scott Paper Company in the 1960s. Preliminary examination of the paper dress revealed that paper rather than textile conservation techniques would be most suitable for its treatment. The dress had previously been folded, resulting in the loss of its original shape. In the exposed areas, heavy brown discolouration could be seen. Fibre microscopy showed chemical woodpulp and revealed that the dress was reinforced with a cellulose acetate thread network. Analysis using the energy dispersive X-ray fluorescence spectrometry showed the presence of zinc, a possible sign that a zinc based fire retardant was used. Different washing methods were considered, the successful method being supporting and interleaving of the dress during washing. Calcium hydroxide followed by magnesium bicarbonate baths were used for deacidification. The heavy discolouration was reduced with a 3% w/v hydrogen peroxide solution. As the surface of the dress had a very definite texture (similar to that of paper towels), special care had to be taken in the handling and drying of the paper dress. Final drying was carried out on a dummy, in order to retain the shape of the dress.

Keywords

Paper conservation, textile conservation, paper dress, 20th-century material, deacidification, bleaching, handling, drying

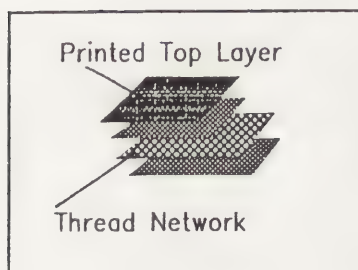


Figure 1. Cross section of the paper.

The Conservation of a Paper Dress from the 1960s: A Case Study

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Introduction

In 1992, the Victoria & Albert Museum acquired a number of paper dresses. The following case study examines the conservation of a 1966 paper dress, manufactured by Scott Paper Company, which required conservation in order to be exhibited in the newly opened 20th-century gallery. Preliminary examination by the textile conservation section showed that the nature of the object required conservation techniques used in paper conservation. Some methods from the field of textile conservation were employed in the actual treatment, especially in re-establishing the original shape of the dress.

A brief history of paper dresses

Paper dresses did not develop from the traditional marketing of fashion. The first paper dresses to be manufactured were produced by the Scott Paper Company in late March 1966; the paper dress discussed in this case study actually came from this production. The intention of the company was to promote, with the help of these paper dresses, a new series of paper napkins, toilet paper, and paper towels. The dresses were sold by mail order for \$1.00 and 25 cents postage and proved to be an immense success. Within five months, the company received orders for over 500,000 items. The dresses were available in different sizes, but in one style only. The design was a black and white Op Art pattern (1). The very nature and intention of the dress being disposable means that very few paper dresses have survived to the present day (2).

Scott Paper Company, therefore, initiated a fashion that touched the nerve of the 1960s. Paper clothing could be manufactured cheaply by mass production. The very low price allowed young people to acquire them easily. The paper dresses gave an experimental forum for fashion and an instant transmission of contemporary ideas. The stiff fabrics highlighted the silhouette and design of the dresses. Paper dresses were a celebration of new technology for a public who wanted to wear "the latest thing."

Condition

Before being acquired by the Victoria & Albert Museum, the paper dress had been stored folded, the folded area being exposed to the atmosphere. This inappropriate method of storage had led to heavy creases, distortion of the overall shape of the dress, and heavy brown discolouration along the exposed areas. This discolouration had disfigured the dress badly.

Fibre analysis

A cross section of the paper dress showed that the structure of the paper consisted of four layers, loosely held together, similar to a kitchen roll paper. Between the second and third layers, a thread network was interleaved, possibly to give the dress more tear resistance (See fig. 1). The thread could be identified as a cellulose acetate. Fibre microscopy showed the presence of chemical wood pulp.

Energy dispersive X-ray fluorescence spectrometry

The washing instruction on the label of the dress suggested that it had been treated with a fire retardant and that washing, dry cleaning, or soaking would

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make the fabric dangerously flammable when redried. Borates, boric acid, and zinc-based salts are known to be used for finishes not fast to washing (3). Energy dispersive X-ray fluorescence spectrometry (EDXRF) examination was carried out to detect if a zinc salt fire retardant had been used on the dress. The molybdenum target primary X-ray source was operated at 49 keV and 0.2 mA with a lifetime of 60 seconds and an airpath. Traces of calcium, iron, and zinc could be found in the white areas of the dress (see fig. 2). These same traces were found in the black areas, but with the addition of titanium. Traces of iron occur in almost all papers, calcium may derive from the addition of chalk, and the presence of titanium implies that it may be a part of the printing ink. The detection of zinc in trace quantities gives strong evidence of a zinc-based fire retardant. Otherwise, it could be present as a whitener or derive from zinc rollers used during processing in the paper factory.

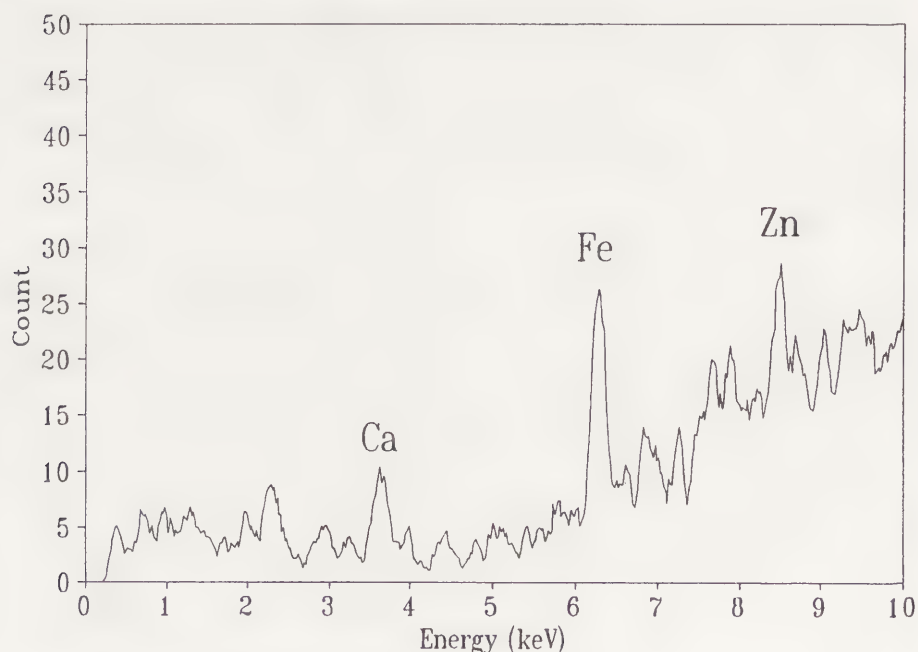


Figure 2. Portion of the EDXRF spectrum.

The pH test

Surface pH-measurement using BDH[®] indicator strips (range 0–6) revealed a pH of 4–4.5 (double checked) (4).

Washing

The colours were tested and found to be stable in water and in solutions of both calcium hydroxide and magnesium hydrogen carbonate (bicarbonate). It was decided to wash the dress in order to reduce the acidity and the brown discolouration products.

Prior to washing, different approaches were considered. In the field of textile conservation a standard washing procedure involves water being applied by means of a shower-spray (or through a watering can rose) (5). This procedure seemed not to be applicable for the paper dress, as the distinct texture of the surface (similar to paper towels) would probably not have withstood this kind of treatment. Another possibility was to place the dress on a dummy and then immerse dress and dummy into a water bath. This approach was not feasible, since the depth of the required bath would have made it very difficult to control or handle the object during the washing procedure.

The following method was applied and proved to be successful. The dress was supported on a heavy weight Bondina[®] (a non-woven polyester web). A second heavy weight Bondina[®] was interleaved between the dress' front and back. A third piece of Bondina[®] was held ready, so the dress could be easily turned from one side to the other.

Deionised water was made slightly alkaline to pH 7–8 with a solution of $\text{Mg}(\text{HCO}_3)_2$. The supported dress was at first relaxed with a very fine water spray and then float washed. Since the dress kept its physical strength and the colours proved to be stable during the first 10 minutes of float washing, it was decided to immerse the dress to increase the washing activity.

The paper dress absorbed water very rapidly. It also tended to retain water. This caused certain difficulties in handling, especially when changing the dress from one bath to another. The water was discharged from the bath and the retained water in the dress was removed with blotting paper, lowering the total weight of the dress. Two pairs of hands were then required to lift the dress out of the bath. Extreme care had to be taken during this procedure, since the paper was still quite heavy due to water retention. It was not possible to blot off all the excess water *in situ* because of the delicate nature of the surface texture. The brown discolouration in the middle of the dress was only slightly reduced. To increase the washing activity, a second bath of warm water (approximately 40°C) was used.

Deacidification

In order to remove any remaining acidity and to deposit a large amount of buffer in the paper, the dress was deacidified in two different baths. For the first bath, calcium hydroxide solution was used (pH 9–10) (6). Calcium hydroxide is thought to swell the fibres, thus reducing discolouration (7). This can diminish the need for bleaching treatment. Deacidification with calcium hydroxide also leads to a high uptake of calcium (8). Magnesium hydrogen carbonate (magnesium bicarbonate) was used for the second bath (preparation as described by M. Hey). Studies by J.C. Williams et al indicate that the presence of magnesium can help prevent transitional metal (e.g., iron) catalysed degradation (9). It is important to inhibit this degradation, which occurs naturally during the ageing cycle of paper, but it is even more important to do so during the oxidative bleaching treatment carried out in this case study. Calcium carbonate does not seem to have this quality.

Hydrogen peroxide bleaching

Although the brown discolouration was reduced by washing and deacidifying, the discolouration continued to disfigure the dress. It was, therefore, decided—in consultation with the curator—to locally bleach the disfigured area.

Hydrogen peroxide was used in a concentration 3% w/v ($1\text{H}_2\text{O}_2$ 30% w/v : 9 deionised H_2O). The pH was adjusted with ammonium hydroxide (NH_4OH) to pH 9. It must be emphasised that the bleaching solution was only used for the duration before the occurrence of bubbles in the solution, to prevent blistering (10). As a result of the volatile nature of ammonia ($\text{NH}_4^+ + ^-\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3\uparrow$), the pH had to be checked regularly to prevent pH drop and the bleaching solution had to be applied in a well-ventilated room.

The dress was slightly moistened by water spray to prevent the creation of haloes and the bleaching solution was then tested in a small area (including a part of the printed area). The bleaching solution was locally applied with a brush. After 15 minutes, the area was dried with a hair dryer to assess the result of bleaching. The test showed a positive result; the staining could be reduced without creating a halo and without affecting the fragile surface of the paper dress or the printed area.

The bleaching treatment was repeated three times and then the dress was washed. The discolouration was removed to a large extent but a fourth and final bleaching was necessary. The dress was then given a final wash and deacidified locally with $\text{Mg}(\text{HCO}_3)_2$.

Drying technique

Both the three dimensional nature of the object and its delicate surface texture posed potential problems for the drying of the paper dress. As previously mentioned, the paper retained considerable amounts of liquid when removed from

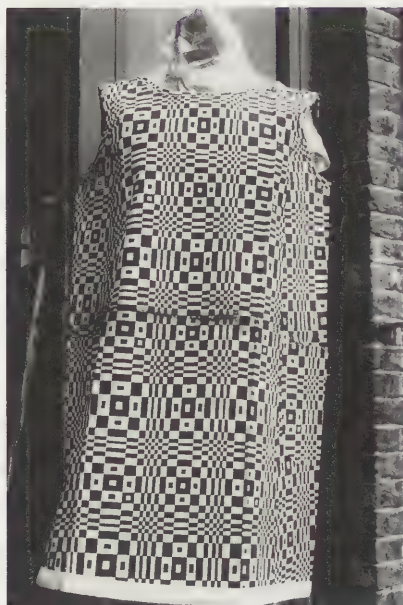


Figure 3. Paper dress, before treatment.



Figure 4. Paper dress, after treatment.

the bath. The paper dress was placed on a pile of fresh blotting paper and, from the top, excess liquid was removed by gently placing fresh blotters on the dress. The blotters from both sides of the dress were changed frequently. The next step was the removal of the support and interleaving support. The damp dress was placed between felts. The felts were not weighted. For the final drying the dress was positioned on a dressmaker's dummy and covered with Lens[®] tissue as a protection against dust from the air. This final drying step allowed the dress to dry without losing its three dimensional shape. Since the distinct texture of the paper did not allow the use of pressure, certain creases could not be totally removed.

Reinforcement and local repairs

There were clear signs on the inside of the dress that it had, in fact, been worn. The inside layer of the dress, in the shoulder areas, was missing due to abrasion. Other areas that would have come into contact with the wearer's body were also abraded. In the areas where the inside layer was missing, lightweight Japanese Kozo paper was used as a replacement. The adhesive used was methyl cellulose, in a concentration of 5% w/v in deionised water. Lightly abraded areas were reinforced with a solution of 1% w/v methyl cellulose in deionised water. Figures 3 and 4 show views of the paper dress before and after treatment.

Conclusion

This case study highlights the approach to the conservation of a three-dimensional, 20th-century paper object. It shows that most of the established techniques in paper conservation could be used and only small modifications had to be introduced. The water washing and the deacidification improved the appearance of the paper dress considerably. Local bleaching proved to be successful in reducing the areas of heavy discolouration. It was impossible to completely remove all the creases due to the delicate surface texture of the dress. This demonstrates the compromise a conservator often has to find between the final aesthetic appearance of the object and the desire not to interfere with its authenticity.

Acknowledgments

The authors would like to acknowledge the help of Jo Darrah, Senior Scientific Officer at the Victoria & Albert Museum, with the fibre analysis and the EDXRF examination. The authors would like to extend thanks to Gerhard Banik, Akademie der Bildenden Künste in Stuttgart, for the exchange of ideas on deacidification and bleaching; David Ford, Assistant Scientific Officer at Victoria & Albert Museum, for the EDXRF graph. Special thanks are offered to Elizabeth Martin, Senior Conservator, Photographs, Victoria & Albert Museum, and Dr. Jonathan Ashley-Smith, Keeper of Conservation, Victoria & Albert Museum, for their encouragement and support.

Materials

BDH[®] Products. Merck-BDH Ltd., Hunter Boulevard, Magna Park, Lutterworth, GB-Leics LE17 4XN, United Kingdom, Telephone +44/800 223 344, Fax +44/455 558 586.

- pH-Indicator strips, range pH 0–6, non-bleeding, no. 31505
- Calcium hydroxide, AnalaR[®] grade, no. 10304, lot 9565270E
- Magnesium hydroxide, general purpose reagent grade (GPR[®]), no. 29076, lot 4990660H
- Methyl cellulose, low substitution, GPR[®] grade, no. 29217, lot 5973330N (viscosity of 2% aqueous solution at 20°C about 400cP)
- Hydrogen peroxide solution, about 30% w/v H₂O₂ GPR[®] grade, no. 28519 6H, lot 5740650M

Bondina[®] (a non-woven polyester web). Bondina Industrial Ltd., Greetland, Halifax, Yorks HX4 8NJ, United Kingdom, or Conservation Resources, Ltd., Units 1, 2 & 4 Pony Rd., Horspath Industrial Estate, Cowley, Oxford OX4 2RD, United Kingdom, Telephone +44/865 747755, Fax +44/865 747035

Lightweight Japanese Kozo Paper. Paper Nao, 1-29-12-201 Sengoku, Bunkyo-Ku, Tokyo 112, Japan

Notes

1. Op Art, the illusion of movement based upon the eye's optic nerve.
2. A. Palmer, "Paper Dresses: the Ultimate in Ready-to-Wear" in *Per Una Storia Della Moda Pronta*, Edifir Edizioni, (Florence, Italy, 1991) 311.
3. W. Garner, *Textile Laboratory Manual* Volume 2 (Heywood Books, London, 1966), 103.
4. Surface pH-measurement reading represents only a relative measurement. Procedure:
1. The paper is moistened with drops of deionised water (to minimise the presence of CO₂ in the deionised water, which makes it slightly acidic, the deionised water is boiled to remove the CO₂. The deionised water is then cooled to room temperature in a closed container). 2. A pH indicator strip is pressed on the wetted surface by means of a glass plate. 3. When the indicator strip no longer shows any colour change (between 1 to 10 minutes contact with the object), the moist strip is compared with the colour chart for the evaluation of the pH.
5. Marion Kite, Senior Conservator, Textile Conservation, Victoria & Albert Museum, personal communication.
6. Stock solution prepared as described by M. Hey in "The Washing and Aqueous Deacidification of Paper," *The Paper Conservator* 4, (1979): 66-80. The stock solution was diluted with deionised water to the desired pH.
7. Gerhard Banik, *Akademie der Bildenden Künste*, Stuttgart, Germany, personal communication.
8. H. Burgess and A. Boronyak-Szaplonczay, "Uptake of Calcium or Magnesium into Seven Papers during Aqueous Immersion in Calcium or Magnesium Solutions" in *Conference Papers Manchester 1992*, S. Fairbrass, editor (London: The Institute of Paper Conservation, London, 1992).
9. J.C. Williams, C.S. Fowler, M.S. Lyon, and T.L. Merrill, *Metallic Catalysts in the Oxidative Degradation of Paper*, *Advances in Chemistry*, Series 164, American Chemical Society, Washington, DC, 1977.
10. H. Burgess, "The Use of Chelating Agents in Conservation Treatments," *The Paper Conservator* 15, (1991): 36-44.

Abstract

The impregnation and absorption behaviour (mass increase) of commercially available methyl cellulose (Methocel A (R), Dow Chemical) as a function of time was investigated for two different modern papers. Newsprint and Whatman filter paper were immersed in methyl cellulose solutions of different viscosity grades and concentrations for different periods. The viscosity grades of methyl cellulose used were 15, 400, 1500, and 4000 mPav.s at concentrations ranging from 0.25% to 1.0%. The study shows that diffusion is the main physical process by which the paper is impregnated and that it is not dependent on paper type. The low viscosity methyl cellulose solutions impregnate both papers to saturation within minutes, whereas the high viscosity methyl cellulose solutions take longer to impregnate both papers to saturation.

Keywords

Methyl cellulose, impregnation, Whatman filter paper, newsprint paper, resizing, Methocel (R).

The Impregnation and Absorption Behaviour of Methyl Cellulose on Two Modern Papers

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South Africa

Introduction

Methyl cellulose is a very popular material amongst conservators in various fields. In book and paper conservation it is used both as an adhesive and as an impregnating material. (In the book and paper conservation community it is referred to as a resizing material.)

Methyl cellulose has been shown to be a permanent (chemically stable) and durable material. Feller and Wilt have demonstrated that the stability of methyl cellulose is excellent and made the following observations: "discoloration after > 1000 hours at 95°C is negligible; weight loss and discoloration at 110°C to 90°C is minimal; resistance to loss of viscosity (decrease in molecular weight) after more than 37 days at 90°C is good; its resistance to degradation by enzymatic action is excellent; and its resistance to acid hydrolysis tends to be greater than that of cellulose itself" (1). This will certainly increase methyl cellulose's already wide popularity and use in the conservation community.

A closely related compound that also demonstrates permanent and durable qualities and is widely used in a similar fashion to methyl cellulose is sodium carboxymethyl cellulose (2).

The use of methyl cellulose and/or carboxymethyl cellulose (CMC) as an adhesive or impregnating material has been the focus of many studies. A brief overview of these studies reveals that as early as the 1960s, CMC was used alone or in combination with a wet strength agent (Kymene), as an impregnating material for paper at concentrations of 1.0% and 2.0% (3). Raff et al. report that the various test papers were not immersed, but were placed between blotters saturated with CMC solutions and rolled with brass rollers at a pressure of 100 PSI (4). Zappala Plossi studied it as an adhesive at a concentration of 3.0% (5). Baker studied both methyl cellulose and CMC as impregnating materials on Whatman filter paper (6). In this case, Methocel (R) A4M (Dow Chemical Co.), Cellulose Gum CMC 7HSP (Hercules, Inc.), and Cellofas B3500 (Imperial Chemical Industries Ltd.) were used at concentrations of 0.5% and 2.5%. Application of the solutions was done by brushing onto only one side of the paper.

Evetts, Lockwood, and Indictor studied a variety of compounds including methyl cellulose on Whatman filter paper (7). The filter paper was immersed for 1–2 minutes in a 0.1% and 1.0% methyl cellulose A15C (Dow Chemical Co.) solution. Ravines, Indictor, and Evetts studied the impregnation effects of methyl cellulose of the different viscosity ranges available, such as A15LV, A4C, A15C, and A4M, (Dow Chemical Co.) at two concentrations (1.0% and 2.5%) on Whatman filter paper (8). The filter paper was immersed for 5 minutes, and for the more viscous solutions it was brushed on only one side of the paper.

Carrapella, Powell, Rutiser, and Barger studied a range of sizes including methyl cellulose at a 0.5% concentration (no mention of the methyl cellulose type is indicated) on book papers ranging from the 18th–20th centuries (9). The latest contribution is a short commentary by Baker on her own earlier study done in

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1984. She comments and raises questions on the possible role the methyl celluloses of different viscosity grades may have in the resizing of paper (10). All the above-mentioned studies used various approaches and application methods, and all conclude that the paper/methyl cellulose or CMC system remains far stronger than the untreated and unaged papers.

Therefore, in an effort to extend the observations of the paper/ methyl cellulose system, this study presents the impregnation and absorption behaviour of methyl cellulose of different viscosity grades on two modern papers, Whatman filter paper and newsprint paper.

Materials and method of application

The paper samples were chosen from Whatman cellulose filter paper grade qualitative grade no. 1 (control number 234/0290/21) and newsprint paper. The Whatman paper characteristics are as follows: composed of pure cotton linters, alpha cellulose; particle retention, 11 afam; ash 0.06%; grammage 87 g/m²; thickness 0.18 mm; loading capacity is normal; and medium retention and flow rate (11). The newsprint paper is composed of chemical and thermochemical wood pulp, with a grammage 48 g/m², and a thickness 0.08 mm. Paper samples were cut into strips in the machine direction to 15 mm wide × 220 mm long (folding endurance of paper (MIT tester), T511 om-83).

The methyl cellulose impregnating agent chosen for this study was Methocel A. It is available from Dow Chemical Company in four viscosity grades (See table 1).

The aqueous methyl cellulose solutions were prepared in various concentrations as recommended in the Handbook of Methocel (12). The concentrations of the aqueous methyl cellulose solutions were chosen to fall within the same viscosity range. For the solutions of all the different molecular weights to fall within a specific viscosity range required that the concentrations decrease as the molecular weight of the methyl cellulose increases (See table 2).

The paper samples were prepared by placing the strips of paper vertically between sheets of polyester non-woven, immersing the non-woven sandwich of paper strips in a fresh aqueous solution for a predetermined length of time, removing the sandwich by holding onto two corners at one end of the sandwich, letting the majority of the solution drain off into the container, placing the sandwich on an angled sheet of Plexiglass (R) to drain for approximately 5 minutes, and then finally hanging the sandwich vertically to air dry.

The immersion times were arbitrarily chosen to range from minutes to hours: 1, 2, 5, 10, 15, 20, 30, 45, 60, 90, 120, and 180 minutes. In a few cases, the samples were left in the aqueous solution for longer periods and overnight. The timing of each immersion interval was started when all of the immersed paper samples had been fully wetted. The timing for full wetting varied for each paper type.

Mass changes

Treated and untreated samples were weighed before and after immersion. A Metler H30 analytical balance with an accuracy of 0.0001 g was used for all mass determinations. The temperature and relative humidity (RH) of the room varied from 22–24°C and 45–60% RH, respectively. Mass changes are reported as mass increase and percentage increase.

Results and discussion

Tables 3A and 3B (Whatman filter paper) and Table 4 (newsprint paper) illustrate how the results were compiled and show the changes in mass: mass increase and percent mass increase of Whatman filter paper and newsprint paper samples in the various methyl cellulose solutions for various time intervals of up to 180 minutes. The range of uncertainty in the mass increase values is based on the standard deviation for the weighings.

The full wetting time varied for each paper type. The full wetting time for

Table 1. Types of Methocel A (Dow Chemical Co.).

Viscosity types in 2% aqueous solutions at 20°C	Viscosity range (mPa·s)
Methocel A15LV	13–19
Methocel A4C	350–550
Methocel A15C	1200–1800
Methocel A4M	3500–5600

Table 2. Methyl cellulose concentrations and viscosity range.

Metho- cel A viscosity type	Concen- trations used (in % w/v)	Approximate viscosity range (mPa·s) @ 20°C
A15LV	1.0%	approx. 5
	2.25%	20–25
A4C	1.0%	25–40
A15C	0.75%	25–40
A4M	0.25%	approx. 5
	0.50%	25–40

Table 3A. Mass (g)^a of Whatman filter paper immersed in 1.0% A4C (28/4/92).

Immersion time (in minutes)	Mass before immersion (in grams)	Mass after immersion (in grams)	Mass increase (in grams)	Percent increase (%)
2	0.2866 ± .0012	0.3055 ± .0013	.0189	6.2
5	0.2779 ± .0010	0.2975 ± .0010	.0196	6.6
15	0.2780 ± .0012	0.2959 ± .0010	.0179	6.1
30	0.2816 ± .0007	0.3006 ± .0009	.0190	6.3
60	0.2826 ± .0010	0.3019 ± .0010	.0193	6.4
120	0.2792 ± .0006	0.2969 ± .0004	.0177	6.0

^a Average and standard deviation of 10 measurements; otherwise, the number of measurements is indicated in parentheses.

Table 3B. Mass (g)^a of Whatman filter paper immersed in 1.0% A4C.

Immersion time (in minutes)	Mass before immersion (in grams)	Mass after immersion (in grams)	Mass increase (in grams)	Percent increase (%)
1	0.2862 ± .0010	0.3045 ± .0011	.0183	6.0
2	0.2746 ± .0007	0.2919 ± .0007	.0173	5.9
5	0.2801 ± .0009	0.2965 ± .0010	.0164	5.5
10	0.2759 ± .0009	0.2899 ± .0010	.0140	4.8
20	0.2871 ± .0009	0.3047 ± .0008	.0176	5.8
45	0.2732 ± .0012	0.2889 ± .0013	.0157	5.4
90	0.2764 ± .0006	0.2920 ± .0007	.0156	5.3
120	0.2775 ± .0007	0.2934 ± .0006	.0159	5.4
180	0.2814 ± .0008	0.2969 ± .0009	.0155	5.2

^a Average and standard deviation of 10 measurements; otherwise, the number of measurements is indicated in parentheses.

Table 4. Mass (g)^a of newsprint paper immersed in 1.0% A4C.

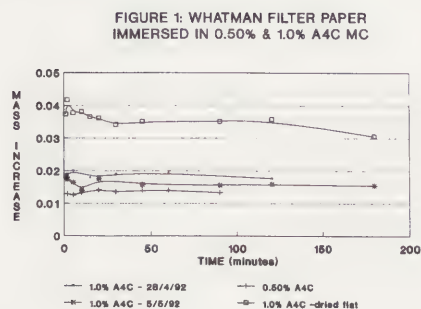
Immersion time (in minutes)	Mass before immersion (in grams)	Mass after immersion (in grams)	Mass increase (in grams)	Percent increase (%)
1	0.1633 ± .0025	0.1687 ± .0025	.0054	3.2
2	0.1639 ± .0021	0.1689 ± .0021	.0050	3.0
5	0.1644 ± .0028	0.1699 ± .0031	.0055	3.2
10	0.1649 ± .0025	0.1688 ± .0024	.0039	2.3
15	0.1648 ± .0022	0.1698 ± .0050	.0050	2.9
20	0.1631 ± .0020	0.1617 ± .0034	.0040	2.4
30	0.1634 ± .0023	0.1648 ± .0023	.0014	0.9
45	0.1577 ± .0020	0.1596 ± .0017	.0019	1.2
60	nv	nv	nv	nv
90	0.1624 ± .0016	0.1637 ± .0016	.0013	0.8
120	0.1685 ± .0018	0.1692 ± .0019	.0007	0.4
180	0.1580 ± .0004	0.1631 ± .0007	.0051	3.1

^a Average and standard deviation of 20 measurements; otherwise, the number of measurements is indicated in parentheses. nv = no value.

Whatman filter paper varied from 8 to 12 seconds for all solutions, and for newsprint paper it varied from 20 to 25 seconds. The timing of the immersion interval was begun once the paper was fully wetted.

Whatman filter paper

Figure 1 summarizes Tables 3A and 3B, and the data for Whatman filter papers immersed in 1.0% A4C solution and dried flat, and for Whatman Filter papers immersed in a 0.50% A4C solution. It shows the mass increases of Whatman filter papers immersed in two concentrations of A4C, an intermediate molecular weight material.



Tables 3A and 3B show the data for two different sets of Whatman filter papers immersed in 1.0% A4C at different times and are described by the date the immersion took place. The results indicate that the experimental approach described above is reproducible.

Figure 1 shows the data for another set of Whatman filter papers immersed in 1.0% A4C, but in this case the non-woven sandwich with the strips was dried flat on a nylon screen. Drying flat apparently does not allow as much drainage as hanging vertically does. Hence, the 2 to 3 fold increase in the mass of the flat dried samples over the vertically dried samples. This is an indication of how much variation can be introduced by changing one simple step in the experimental design. The final curve in Figure 1 summarizes the data for Whatman filter papers immersed in 0.50% A4C.

For the Whatman filter papers immersed in the higher concentration solution, 1.0% A4C, there was greater absorption by approximately half of that of the lower concentration, 0.50% A4C. The time it takes to reach saturation in a 1.0% A4C solution appears to be between 10 to 20 minutes (Table 3A), and for the second sample set (Table 3B) the time to saturation appears to be under 2 minutes. For the 0.50% A4C solution the time to saturation appears to be under 1 minute. In this A4C set, the two tendencies observed are that the higher the concentration of the solution the greater the impregnation/absorption by the paper, and the higher the concentration of the solution the longer the time required for the methyl cellulose to diffuse into and saturate the paper.

Figure 2 summarizes Tables 3A and 3B showing the mass increases of Whatman filter papers for the lowest molecular weight material, A15LV, in two concentrations, 1.0% and 2.25% over time intervals of up to 180 minutes. For Whatman filter paper the impregnation/absorption of the higher concentration solution, 2.25% A15LV, is greater by approximately four times than that of the lower concentration solution, 1.0% A15LV. The length of time for the paper samples to reach saturation is under one minute for the lower concentration (1.0%) and about 5 to 10 minutes for the higher concentration (2.25%). Again, the tendencies are the same as those observed in the A4C set: the higher the concentration of the solution, the greater the impregnation/absorption by the paper, and the higher the concentration of the solution the longer the time for the solution to diffuse into and saturate the paper.

Figure 3 summarizes the mass increases of Whatman filter papers for all the molecular weights of methyl cellulose solutions at similar viscosity ranges (25–40 mPa·s, Table 2) over intervals of up to 180 minutes.

Figure 3 shows that the mass increases for the Whatman filter paper samples are greatest for the lower molecular weight material (A15LV), and the mass increases for the other paper samples decreases with increasing molecular weight: A15LV > A4C > A15C > A4M. The time for the paper samples to reach saturation in a 2.25% A15LV solution is approximately 5 to 10 minutes, as was described earlier; for the 1.0% A4C, the time to saturation appears to be between 10 to 20 minutes; for 0.75% A15C it is after 45 minutes; and for 0.50% A4M, it appears to continue to absorb up to 180 minutes.

While maintaining a constant viscosity for every solution, the order of mass increase observed for the Whatman filter paper/methyl cellulose system in Figure 3 reflects the concentrations of the solutions: the more concentrated, the greater the amount of material impregnated/absorbed by the paper. In two previous studies on the paper/methyl cellulose system, it was observed that with methyl cellulose solutions of different molecular weights (A15LV, A4C, A15C, A4M) at concentrations of 1.0% there is a tendency for the Whatman filter paper to have a greater mass increase as the molecular weight of the methyl cellulose solution increased (13, 14).

Newsprint paper

Figure 4 summarizes the mass increase of newsprint paper for the lowest molecular weight material, A15LV, in two concentrations, 1.0% and 2.25% over time intervals of up to 180 minutes. In this case, two sets of newsprint paper

FIGURE 2: WHATMAN FILTER PAPER IMMERSED IN 1.0% & 2.25% A15LV MC

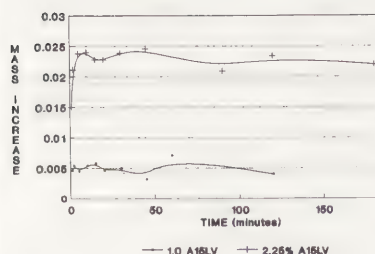


FIGURE 3: WHATMAN FILTER PAPER IMMERSED IN A15LV, A4C, A15C, A4M MC (Viscosity of MC is constant)

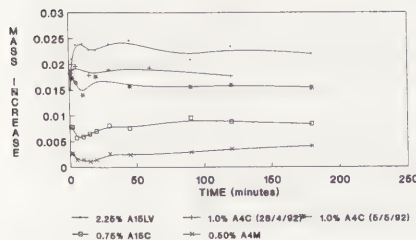


FIGURE 4: NEWSPRINT PAPER IMMERSED IN 1.0% & 2.25% A15LV MC

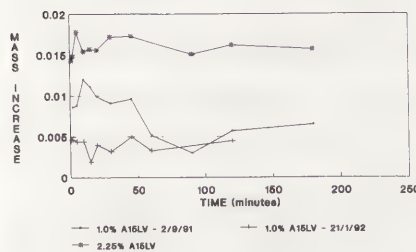


FIGURE 5: NEWSPRINT PAPER
IMMERSED IN 0.25% & 0.50% A4M MC

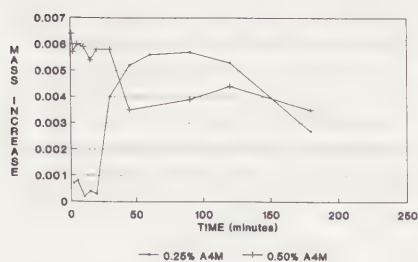


FIGURE 6: NEWSPRINT PAPER
IMMERSED IN A15LV, A4C, A15C & A4M MC
(Viscosity of MC is constant)

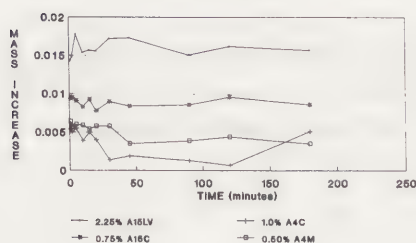


FIGURE 7: WHATMAN & NEWSPRINT PAPER
IMMERSED IN 1.0% & 2.25% A15LV MC

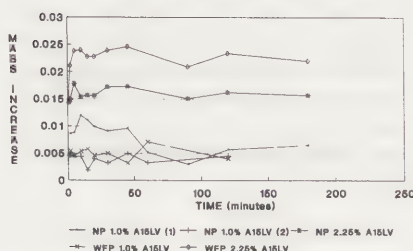


FIGURE 8: WHATMAN & NEWSPRINT PAPER
IMMERSED IN 1.0% A4C MC

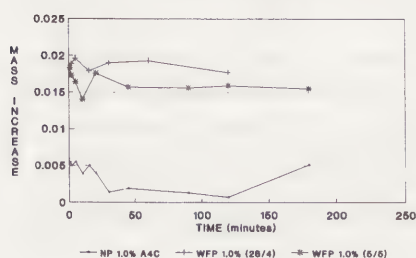


FIGURE 9: WHATMAN & NEWSPRINT PAPER
IMMERSED IN 0.75% A15C MC

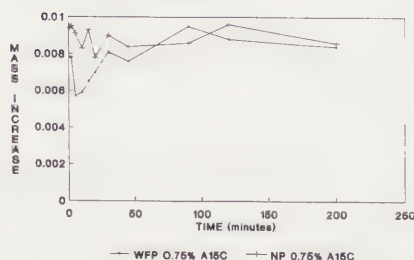
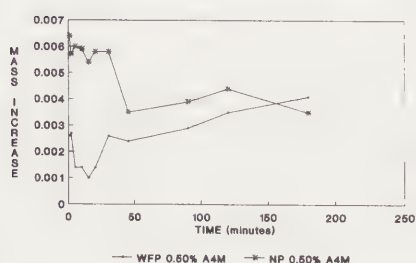


FIGURE 10: WHATMAN & NEWSPRINT PAPER
IMMERSED IN 0.50% A4M MC



samples were immersed in 1.0% A15LV at different times and are described by the date the immersion took place, on 2/9/91 and 21/1/92. The results of these two immersions differ considerably: the 2/9/91 set starts high then drops and levels off after an hour, whereas the 21/1/92 set is constant from the first minute on. This behaviour coupled with the observation of considerable discoloration of the 2/9/91 solution seems to indicate that the batch of newsprint paper chosen and used may not have been homogeneous and probably had a water-soluble component that was dissolving into the solutions. In the 1.0% A15LV-2/9/91 case, there appear to be two physical processes occurring: the diffusion of the methyl cellulose into the paper as well as the dissolution and outward diffusion of a water-soluble component in the newsprint paper.

The impregnation/absorption of the higher concentration solution, 2.25% A15LV, is greater by approximately three times than that of the 1.0% A15LV-21/1/92 set. The time required to reach saturation is under 1 minute for the lower concentration solution, 1.0% A15LV-21/1/92, and 5–10 minutes for the higher concentration solution, 2.25% A15LV.

Figure 5 summarizes the mass increase of newsprint paper for the highest molecular weight material, A4M, at two different concentrations, 0.25% and 0.50%, over time intervals of up to 180 minutes. The newsprint paper in the higher concentration solution, 0.50% A4M, displays similar behaviour to the 1.0% A15LV-2/9/91 set: the samples are losing a water-soluble component and it takes approximately 30–45 minutes for it to dissolve and diffuse out into the solution. (Considerable discoloration of this solution was also observed.) The newsprint paper in the lower concentration solution, 0.25% A4M, is saturated after approximately one hour, but after 2 hours it begins to decrease and at 3 hours it is at half of its maximum impregnation/absorption value. After reaching saturation, the lower concentration solution, 0.25% A4M, has absorbed almost two times more material than the higher concentration solution, 0.50%. This does not show the same concentration dependent trend seen in the lower molecular weight material.

Figure 6 summarizes Table 4 and shows the mass increase of newsprint paper for all the molecular weights of methyl cellulose solutions at similar viscosity ranges (25–40 mPa·s, Table 2) over intervals of up to 180 minutes.

Figure 6 shows that the mass increase for the newsprint paper samples is greatest for the lowest molecular weight material (2.25% A15LV), followed by 0.75% A15C, 0.50% A4M, and 1.0% A4C. Assuming that the end of the outward diffusion of the water-soluble component in the newsprint paper is the same as the length of time to saturation, then the saturation times are approximately 5 minutes for 2.25% A15LV; 30 minutes for 1.0% A4C; and 45 minutes for 0.75% A15C and 0.50% A4M.

Comparison between Whatman filter and newsprint papers

The comparison of both papers immersed in 1.0% and 2.25% A15LV solutions is described in Figure 7. It is interesting to note that the impregnation behaviour of the two papers at 1.0% concentration is practically identical. At the higher concentration, 2.25%, the impregnation behaviour or shape of the curves is similar and the Whatman filter paper is slightly more absorbent than the newsprint.

Figure 8 compares both papers immersed in 1.0% A4C solution. In this case the newsprint and Whatman filter papers are dissimilar. This is the only case in which the values are drastically different. It leads us to believe that the newsprint data is not representative of what is happening and also indicates how important the preparation of the paper samples is.

Both papers immersed in 0.75% A15C solution are compared in Figure 9. As in the 1.0% A15LV case, the impregnation behaviour of the two papers is practically identical.

Finally, Figure 10 compares both papers immersed in 0.50% A4M solution. The impregnation behaviour shown is similar after 45 minutes, the curves level off

after this time and they appear to have reached saturation. The Whatman filter paper shows a gradual increase until it levels off and the newsprint shows a decrease until it levels off. As was described earlier, it appears that a water-soluble component in the newsprint is dissolving and diffusing outward as the methyl cellulose is diffusing into the paper and accounts for the high initial values.

Conclusions

In this study of the impregnation/absorption behaviour of methyl cellulose on two modern papers, we have described the diffusion of methyl cellulose into two modern papers.

The newsprint and Whatman filter paper/methyl cellulose systems can be reasonably described and understood in terms of mass increase and length of time to saturation. The Whatman filter paper/methyl cellulose system is clean and would seem to represent an ideal situation, and the newsprint paper/methyl cellulose system is more complex in that two physical processes are apparently taking place simultaneously: dissolution and outward diffusion of the water-soluble component, and inward diffusion of the methyl cellulose.

It is quite interesting to observe the close similarities between the two paper/methyl cellulose systems in mass increases, the shape of the curves and the saturation times, as shown in Figures 7, 9 and 10. This illustrates that diffusion is the main physical process by which the paper is impregnated and that it is not dependent on paper type, be it filter paper made from cotton linters or newsprint paper made from chemical and thermomechanical wood pulp.

The above information should be of interest and use to book and paper conservators. Considering the many factors in deciding whether there is a need to impregnate (resize) a paper item, the saturation times described in this study should provide the practising conservator with a measure of the time required for immersion treatment in a methyl cellulose solution, since the diffusion of methyl cellulose into paper is not dependent on paper type.

Further investigation

It should be stated that not all the criteria for the utility of impregnating agents have been considered in this study. For instance, physical and chemical tests have not been performed, but should be to better describe the behaviour observed with the mass increases for both Whatman filter and newsprint papers. Another interesting aspect that was not addressed is the effect of artificial or accelerated aging on the impregnated papers.

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Abstract

This study concerns the effects of solvent treatment methods on fibers and pigments, and examines the manner in which fibers and pigments behave and respond to floating and immersion. We know of the beneficial and rejuvenating effects of the universal solvent, water, on the structure and aesthetic appearance of works on paper. But little is known of what happens on the paper surface or in the paper's fiber network during treatment procedures. This research tries to provide answers. Our observations during cold and hot water experiments gave rise to concerns regarding certain traditional treatment methods.

Keywords

Microscopy, "sizing effect," cold and hot water experiments, air drying

Microscopic Examination of Works of Art on Paper during Solvent Treatments in Order to Determine Their Effects on Fibers and Pigments—A Joint American-Romanian Research Project

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Introduction

When a paper conservator treats a work of art on paper, the object already may have experienced a history of poor storage and display conditions, negligent handling, climatic adversities, and a generally harmful environment. Furthermore, if the conservator is dealing with a print or watercolor, the paper's anisotropic behavior will have undergone alterations.

Regardless of the condition of a paper artifact, the conservator is expected to undo years of accumulated damage and, it is hoped, transform a battered looking piece into one that is sound and esthetically pleasing. Yet, even with the best intentions, most if not all conservation treatments call for more handling and intervention which inevitably affect fibers and pigments.

The purpose of our work is to draw attention to the fact that if during treatment we do not see any changes on the paper surface, this does not necessarily mean that no changes have occurred. By working with a microscope, we may be able to see what the naked eye fails to detect.

Our first study involving the microscopic examination of works of art on paper dealt with dry cleaning treatment methods (1). Through microscopic examination we found that alterations and losses had occurred, undetected by the naked eye. This supported our hypothesis that minute changes, multiplied over the treated surface, could have an effect on the overall impression and thus change the integrity and aesthetic appeal of a work of art on paper.

During the second phase of our work, we investigated the effects of solvent treatment methods on fibers and pigments. We wanted to find out how fibers and pigments responded to floating and immersion experiments. We were aware of the beneficial, rejuvenating effects of the universal solvent, water, on the structure and overall appearance of paper and of the immersion baths in other solvents that are sometimes required. With the exception of one experiment with ethyl alcohol, all experiments were carried out with cold and hot water.

Papers and media tested

We examined plain papers of varying quality and degrees of sizing, dating from several centuries. These samples included a lithograph, an etching, an aquatint, a drypoint etching, and a watercolor painting. The artworks were selected from the student days of co-author Yvonne Efremov.

Having demonstrated the extent of surface disturbance during dry cleaning, we selected materials that did not require prior dry cleaning treatment.

Procedures

The test samples were divided into equal sections. A record was kept for each experiment.

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- 1) Control sample
- 2) Ethyl alcohol (99% solution)
- 3) Cold water
- 4) Cold water; hot water
- 5) Cold water; buffer solution (magnesium bicarbonate, pH 8.5)
- 6) Cold water; hot water; buffering solution (magnesium bicarbonate, pH 8.5)
- 7) Cold water; bleaching solution (sodium chlorite, 2%); rinsing; buffering solution (magnesium bicarbonate, pH 8.5)
- 8) Cold water; hot water; bleaching solution (sodium chlorite, 2%); rinsing; buffering solution (magnesium bicarbonate, pH 8.5)

We used tap water at room temperature, ranging from 22 to 25°C, depending on the outside temperature. The hot water experiments were carried out at 45–55°C. The pH of the water measured 6.7–7, as indicated by Merck pH measuring sticks (pH 0–14 and pH 6.0–9.0). We determined the type of size with iodine solution (LUGOL), J+JK test for starch, ninhydrin and ink tests for gelatin, and ethyl alcohol test for rosin size. The Romanian authorities provided a SM-210 Carl Zeiss (Jena) microscope for our use.

Experiments and results

The sample that had received the most treatment was compared with the control sample. Each sample was examined under the microscope before and after each treatment.

Plain Papers

We began our experiments with plain papers for two reasons: 1) the papers at our disposal carrying various media did not offer sufficient variety for our purposes, and 2) we wanted to familiarize ourselves with the reactions of plain paper to a series of aqueous treatment methods.

We selected the following well-preserved plain papers:

- 1) Handmade, laid, hard gelatin sized, watermark "F.J. HEAD & CO"
- 2) Handmade, laid, slack sized, starch sized
- 3) Machine made, laid, hard starch sized, 20th century
- 4) Machine made, wove, slack sized (size not identified), watermark "J. PERIGORD"

Microscopic examination of these papers before treatment, in their dry state, showed an undisturbed surface with few to very few undisturbed fibers. We decided on floating as the first aqueous experiment.

After cold water floating, we observed that initially loose, disturbed fibers had moved to an upright position. We also observed that very short fibers, previously undisturbed, had lifted themselves to an upright position. The fibers moved upward as soon as they had absorbed water.

Following air drying, some fibers tended to settle into an oblique position, while some continued to remain in a vertical position. They did not return to their original orientation of lying just above the surface. In order to better understand this phenomenon, we refloated the samples in cold water before the hot water and buffering experiments. Each time the fibers lifted themselves up and remained in a vertical position. However, when immersed, the waterlogged surface revealed fewer lifted fibers. As the water evaporated, fibers began to lift.

Media

We hypothesized that experimenting with pigmented paper might yield different findings. The most interesting observations of our experiments on four preparations are discussed.

The first preparation was a rosin-sized lithograph on wove paper with slack starch. The visual and microscopic examination of the fibers and pigment before treatment showed an undisturbed surface. Microscopic examination of the still damp samples that had floated in cold water revealed three phenomena: uninked

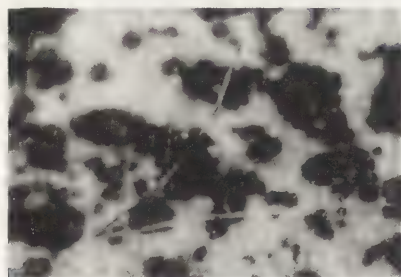


Figure 1. Lifting of partly inked fibers in inked and uninked areas (magnification 60 \times).

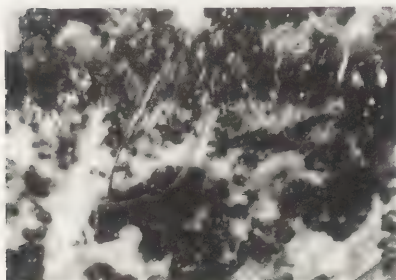


Figure 2. Lifting of inked fibers in inked areas (magnification 60 \times).

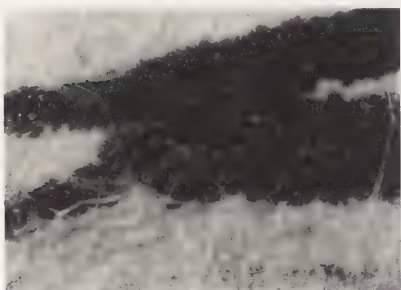


Figure 3. Uninked fibers above pigmented areas (magnification 60 \times).

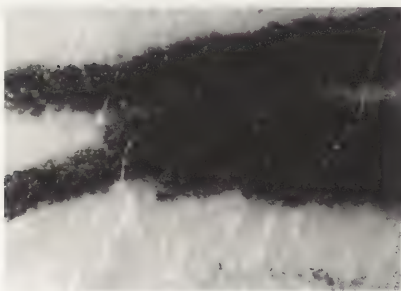


Figure 4. Surface in damp state (magnification 60 \times).

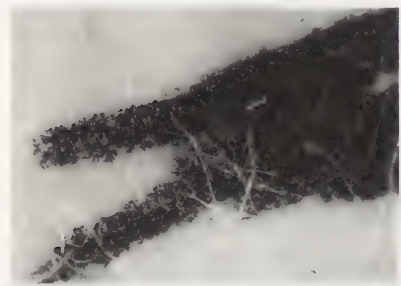


Figure 5. Surface in dried state (magnification 40 \times).

fibers lifted in uninked areas; partly-inked fibers lifted in inked and uninked areas (See fig. 1); and inked fibers lifted in inked areas (See fig. 2). The last case was observed less frequently than the first two cases. We then compared the state of a floated sample with that of an immersed sample to see whether the fibers and pigments reacted differently. Under the microscope, the floated sample showed more fibers lifted than the immersed sample. None of the fibers lifted were visible to the naked eye.

The second preparation was an etching and aquatint on Japanese waterleaf paper. While the pigmented surface was intact, long, uninked fibers were lying loosely above the pigmented areas (See fig. 3). The floated samples absorbed water immediately; the waterlogged paper was too weak for handling without support. Examination of the damp paper following floating showed an undisturbed surface, except for some short uninked fibers which had moved upward and remained upright (See fig. 4). (The long, uninked fibers also had lifted obliquely.) Examination after air drying showed that the uninked fibers had shifted and resettled above the pigmented areas (See fig. 5). The pigmented areas remained undisturbed after all treatments. One observation in particular sparked our interest. During a refloating experiment of these same waterleaf samples several months later, we observed that they were absorbing water much more slowly, even resisting water penetration. These samples, which during the first floating experiment were too weak for handling, now could be lifted out of the water manually, without any support. Aqueous treatment seemed to have strengthened the fiber network.

The third preparation was a drypoint on heavy wove paper with long fibers and hard size (probably gelatin). Microscopic examination of the control sample revealed an irregular surface with loose fibers crisscrossing the image. The pigmented areas were affected, showing white grooves where the inked fibers had lifted (See fig. 6). Examination of the floated cold water sample showed a noticeably more disturbed surface, with additional blank and pigmented fibers standing upright and the drypoint lines no longer intact (See fig. 7). After immersion, we observed fewer disturbed fibers in the heavily inked areas of the waterlogged surface than in the lightly inked and more lightly printed areas. In the latter, loose pigmented fibers were seen floating on the water right above their respective grooves. After evaporation, these fibers remained suspended in the same place. Following air drying, the fibers that had stood upright while waterlogged remained upright (See fig. 8).

This particular sample was then treated with a buffering solution (magnesium bicarbonate, pH 8.5). Upon removal from the buffering solution, we noticed fugitive pigment floating in the solution. We tested the still damp pigmented surface with alkaline tissue paper, and under the microscope observed pigment particles as well as inked and partially inked fibers on the alkaline tissue paper.

The fourth preparation was a watercolor and tusche drawing from the early 1950s on heavy, hard rosin size paper. Under the microscope, the surface appeared undisturbed. The pigmented areas looked glossy, with more gloss on concentrated pigments. Some tusche lines were brittle and flaky (See fig. 9). During cold water floating, perspiration drops were observed on the pigmented areas. Fibers had lifted during floating and were standing upright, especially in the open and lightly pigmented areas. During the buffering experiment, we observed increased perspiration. But very few fibers lifted. The cracked tusche fragments appeared to have been pushed upward by the swelling of the fiber network, regaining their original position after air drying. Upon comparing the experimental samples with the control sample, we observed that the original watercolor gloss had disappeared from the surface after our experiments and looked dull.

Sizing effect

It was clear to us that the papers would react differently to aqueous treatment methods. What we were not prepared for and what caught our attention was the realization that samples of the same sheet of paper responded differently to identical, repeat experiments.

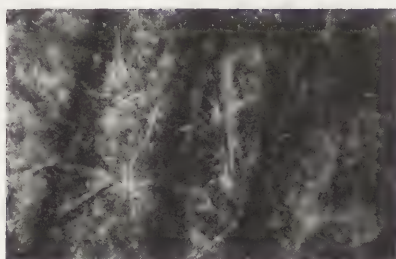


Figure 6. White grooves underneath inked fibers (magnification 40×).

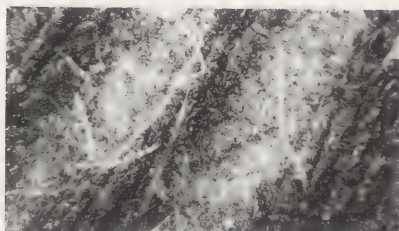


Figure 7. Surface after floating (magnification 60×).



Figure 8. Upright fiber following air drying (magnification 60×).

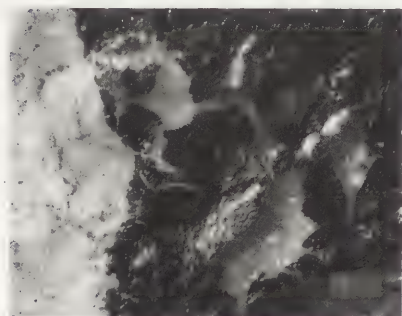


Figure 9. Flaky tusche lines (magnification 40×).

During the cold water floating experiment with plain handmade hard gelatin sized paper, the samples relaxed after ten minutes and only then began to absorb water. A 15-minute immersion followed; upon removal from the water, the paper looked translucent, with the exception of some opaque areas.

During a subsequent hot water floating experiment, the air dried samples curled up immediately, then slowly relaxed. After 30 minutes of floating, they began to absorb water, but only in the form of tiny, translucent dots which resembled pin dots. The rest of the paper remained opaque. The hot water seemed to have caused rapid swelling of the fibers and sizing, preventing the liquid from penetrating completely into the fiber network, except for the areas covered by pin dots. During a second cold water floating experiment, the sample curled up even more rapidly, almost violently. This reaction diverged from the first cold water floating experiment. After relaxation of the paper, water penetrated very slowly across the verso, spreading over the entire sample in large clusters. We gathered from this observation that the first cold water experiment may have affected the distribution of sizing. During repeated hot water experiments, water penetrated the sizing only in the form of the aforementioned tiny pin dots. We observed the same behavior during buffering experiments.

These observations would confirm Marjorie Cohn's findings that "a regeneration of existing sizing agents [however small] may take place during float washing and immersion and develop a resistance to wetting" later on (2).

The same phenomena were observed during experiments with plain, handmade, slack starch sized paper. During the first cold water floating experiment, the samples remained flat on the water surface, the liquid penetrating immediately. During a second cold water floating experiment, the samples curled, relaxed slowly, and absorbed water very slowly and irregularly.

We also repeated the hot water floating experiment. Whereas absorption was immediate the first time, the sample during the second experiment turned into a "U" before relaxing and absorbing the liquid very slowly. In other words, this slack-sized paper, after cold and hot water experiments, had developed a "sizing effect" and during subsequent solvent treatments no longer absorbed liquids as readily as the first time. We observed this sizing effect in all hard and slack sized papers tested. We observed something like a "regeneration of existing sizing agents" during our experiment with the aquatint etching on long fiber waterleaf Japanese paper. This paper which almost fell apart during the first cold water floating had developed a marked increase in strength during the second cold water floating experiment. We did observe an increase in curling after each aqueous experiment, from a gentle bending or curl during the first cold water floating to sudden curls into tight rolls and "U" shapes, as we repeated float washing experiments later on.

Ethyl alcohol treatment

All samples that were put in a bath of ethyl alcohol dropped immediately to the bottom of the dish. Upon immediate removal, they were stiff and resembled tracing paper. After evaporation of the ethyl alcohol, their physical aspect most closely resembled that of the control sample. When we subjected the alcohol-treated samples to cold water floating, they resisted water penetration for many hours.

Conclusion

We compared the control samples with those that had undergone treatments and observed that:

- surfaces of treated samples showed more visible and pronounced contours (valleys and elevations) which could be seen by the naked eye;
- fibers initially observed as upright before treatment remained upright throughout treatment; loose fibers which lifted during treatment and remained upright after air drying ultimately settled and rearranged themselves above the surface;
- a reduction or loss of starch and gelatin size had taken place after treatment with warm to hot water, buffering solution and bleaching treatment; in

comparison, cold water treatments appeared to maintain, if not improve, the condition of size.

Just as we realized during our study on dry cleaning methods the importance of selecting the right tools for the benefit of the artifact, we have been able to confirm the beneficial effects of aqueous treatment, finding that most types of paper seem to improve from contact with water at room temperature, while the experiments with water at elevated temperatures gave us cause for concern.

Acknowledgments

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Résumé

L'élimination des taches peut être obtenue à l'aide de différents oxydants dont l'application doit être réalisée localement, loin des zones d'écriture, sur table à vide. Cependant si des ions métalliques et particulièrement Fe^{2+} ou Cu^{2+} sont présents, même à l'état de traces, le peroxyde d'hydrogène peut provoquer une dépolymérisation du collagène par des mécanismes mettant en jeu des réactions radicalaires.

Des essais d'inhibition basés sur l'utilisation de complexants des métaux ou d'inhibiteurs de radicaux libres ont été entrepris. L'EDTA utilisé avant et pendant le blanchiment pourrait constituer une possibilité de protection. Mais des essais de vieillissement à la lumière, dont les résultats restent à vérifier, montrent qu'une détérioration post-traitement est possible.

Mots-clefs

Parchemin, nettoyage, dégradation, peroxyde d'hydrogène, ions métalliques, EDTA, vieillissement artificiel

Elimination des taches sur le parchemin à l'aide de peroxyde d'hydrogène: premiers résultats

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Introduction

L'élimination des taches peut être obtenue à l'aide de différents agents de blanchiment chimiques, des oxydants le plus souvent. Cette opération doit être réalisée localement, loin des zones d'écriture, en utilisant une table à vide. Parmi les différents composés que nous avons expérimentés, de bons résultats ont été obtenus avec la chloramine T et le peroxyde d'hydrogène, l'efficacité ayant été estimée visuellement.

Nous avons rejeté l'utilisation de la chloramine T parce qu'il est impossible d'éliminer complètement ce composé du matériau, même après un traitement anti-chlore (borohydrure ou thiosulfate de sodium). De plus un très long rinçage à l'eau courante qui serait nécessaire est tout à fait incompatible avec le matériau.

De ce fait nous avons choisi le peroxyde d'hydrogène pour le nettoyage (1), en utilisant des solutions de concentration allant de 0,3 à 5% maximum. La concentration de ce composé ne doit pas être trop élevée, car cela risque de décolorer le fond en même temps que la tache. Il est donc indispensable de commencer par une faible concentration, qui peut être augmentée peu à peu si nécessaire.

Cependant l'utilisation du peroxyde d'hydrogène peut poser un problème si des ions métalliques, même à l'état de traces, et particulièrement Fe^{2+} ou Cu^{2+} sont présents dans le milieu : ils provoquent une dépolymérisation de la protéine, pouvant conduire à la dissolution totale. Plusieurs chercheurs ont étudié ce phénomène, notamment Clara Deasy qui a travaillé sur cuir et collagène, et ont proposé différents mécanismes mettant en jeu des radicaux libérés par le système $\text{H}_2\text{O}_2 - \text{M}^{2+}$. La détérioration est différente de celle produite par le peroxyde d'hydrogène seul (2).

Nous avons entrepris une étude sur le parchemin, afin de voir s'il était possible de rendre cette méthode inoffensive pour le matériau. Le traitement est en effet efficace et donc utilisé par certains restaurateurs qui ne peuvent savoir si du fer ou du cuivre sont présents dans les manuscrits. Les premiers résultats de cette étude sont présentés ici.

Détermination de la teneur en fer et en cuivre dans les parchemins

Les analyses ont été réalisées sur des cendres de parchemin, en spectrométrie d'absorption atomique. Dans des parchemins modernes, nous avons trouvé des valeurs de 70 ppm de fer et de 3 ppm de cuivre et dans les quelques parchemins anciens mis à notre disposition, des valeurs proches de 250 ppm de fer et de 20 ppm de cuivre, dans des zones ne portant pas d'écriture. La littérature mentionne des valeurs plus importantes dans les parchemins anciens pouvant atteindre des teneurs exceptionnelles de 800 ppm (3).

Il nous est donc apparu indispensable de fabriquer des éprouvettes à partir de parchemin neuf, afin de posséder un lot homogène d'échantillons d'étude contenant des quantités suffisantes de métal.

Choix des tests pour évaluer la dégradation

Perte de masse du matériau ΔM

L'expérience a été menée sur des échantillons d'environ 5g qui ont été pesés jusqu'à poids constant après séjour en atmosphère à thermohygrométrie contrôlée.

Teneur en azote solubilisé au cours du traitement

Ce dosage a été réalisé par la méthode Kjeldahl en récupérant tous les bains et toutes les eaux de rinçage.

Mesure de la température de dénaturation, T_d

Elle a été réalisée en calorimétrie différentielle à balayage. Les deux premiers tests permettent d'évaluer la dissolution de la protéine. D'autre part un abaissement de T_d traduit des modifications au niveau des liaisons dans la molécule de collagène.

Mise en évidence de la détérioration

Pour reproduire la détérioration du parchemin nous avons procédé selon deux voies. Tout d'abord, des échantillons ont été immergés dans des solutions contenant H₂O₂ et des sels métalliques (nous avons travaillé avec Fe²⁺ et Cu²⁺).

Dans une deuxième série d'expériences, les parchemins ont préalablement été traités par une solution de sulfate ferreux ou cuivrique, traitement conduisant à une fixation du métal sur le collagène. D'après des analyses en absorption atomique, nous avons calculé qu'environ 60% du cuivre contenu dans la solution était fixé par le parchemin (pour le fer la fixation est probablement plus importante). Ces résultats seront ultérieurement vérifiés. Après un rinçage soigneux à l'eau courante, les parchemins ont été immergés dans des solutions de H₂O₂.

Nous avons observé une détérioration du parchemin dans les deux cas, ce qui peut laisser supposer qu'une fraction du métal fixé passe en solution et donc qu'une partie des liaisons avec le collagène sont rompues. Il nous reste cependant à mesurer les quantités de métal dissous. La détérioration augmente avec la concentration de H₂O₂, la concentration de M²⁺, le temps de contact et la température. Elle est beaucoup plus importante avec le cuivre qu'avec le fer.

Essais d'inhibition de la réaction de détérioration

L'expérimentation a été menée sur des éprouvettes contenant du cuivre qui, produisant plus de dommage, permet de mieux évaluer le comportement du matériau aux différents traitements. Nous avons préparé des éprouvettes contenant environ 600 ppm de cuivre et travaillé avec une solution de H₂O₂ à 5% qui représente la concentration maximum tolérée par le parchemin. D'après les différents travaux relevés dans la littérature (2, 4, 5), deux voies semblent possibles pour s'opposer à la dégradation du collagène : la complexation du métal et l'interception des radicaux libres.

Utilisation d'agents complexants

Nous avons expérimenté les composés suivants dont l'innocuité a d'abord été vérifiée sur le parchemin seul: EDTA (sel disodique de l'acide éthylène diamine tétracétique), imidazole, Irganox MD 1024® (désactivateur de métaux utilisé dans l'industrie pour stabiliser le polypropylène en présence de cuivre), citrate d'ammonium, cupferron, acide malonique. Ils ont été ajoutés en excès par rapport aux quantités stoechiométriques avant le traitement au peroxyde d'hydrogène. L'Irganox MD 1024® étant insoluble dans l'eau, il a été utilisé en solution éthanolique. Nous avons observé que l'imidazole et l'Irganox MD 1024® étaient tout à fait inefficaces pour protéger le parchemin et que le citrate d'ammonium, le cupferron et l'acide malonique augmentaient encore la dégradation en présence du système H₂O₂ - M²⁺.

C'est l'EDTA qui s'est révélé le plus efficace, bien que cette efficacité ne soit pas très élevée, comme le montre le tableau ci-dessous:

Nous avons pris en considération l'azote provenant des agents complexants pour calculer sa teneur dans les bains et les eaux de rinçage.

Une analyse en absorption atomique a révélé que du cuivre subsistait dans le parchemin après traitement par les agents complexants, montrant que ces derniers n'extraient pas complètement le métal de la protéine.

Tableau I. Inhibition de la détérioration à l'aide d'agents complexants.

$\text{Cu}^{2+} \approx 600 \text{ ppm}$		ΔM	N_2 soluble
H_2O_2 5%	(3 h)	64,8%	8,7%
1. EDTA	(1 h)		
2. H_2O_2 5%	(3 h)	38,0%	5,5%
1. EDTA	(1 h)		
2. H_2O_2 5% + EDTA	(3 h)	9,0%	1,0%
1. Irganox	(3 h)		
2. H_2O_2 5%	(1 h)	50,5%	6,5%

Dans le but d'augmenter l'efficacité de l'EDTA qui nous paraissait être le plus prometteur, nous l'avons utilisé également pendant le traitement au peroxyde d'hydrogène, procédant ainsi en deux étapes:

1er bain: EDTA seul pour la complexation.

2ème bain: EDTA ajouté à H_2O_2 pendant le blanchiment.

Signalons que l'addition d'EDTA ne s'oppose pas au nettoyage.

Dans ce cas, le parchemin est moins détérioré, bien que la protection ne soit pas encore complète, comme l'indique le tableau I. Cependant, nous avons observé qu'en augmentant la durée du premier bain, on obtenait un meilleur effet protecteur, probablement par amélioration du pouvoir complexant. Par exemple, sur un autre parchemin (tableau II) la perte de masse passe de 6 à 2,2 % en allongeant le temps de 1 à 3 heures.

Tableau II. Influence de la durée du 1er bain de complexant sur la protection.

	Parchemin protégé				non protégé
	1 h	2 h	3 h	4 h	—
EDTA					
+					
H_2O_2 et EDTA	3 h	3 h	3 h	3 h	3 h sans EDTA
ΔM %	6,0	3,2	2,2	2,2	75,6
N_2 sol. %	0,5	0,14	<0,1	<0,1	9,9

Ce résultat est assez satisfaisant si l'on considère que de la matière est solubilisée quand on immerge le parchemin dans l'eau (de l'ordre de 2 %), solubilisation due à des composés divers, protéiques ou minéraux.

D'autre part, le parchemin contenant environ 14 % d'azote, le rapport $\Delta M/\text{N}_2$ devrait être proche de 7. Les rapports calculés d'après nos valeurs ne sont pas très éloignés de la valeur théorique si l'on tient compte des erreurs expérimentales, sauf dans les cas où la détérioration est faible. Quand elle est forte, la perte de masse est due essentiellement à la dissolution de la protéine et, pour une faible part, à divers autres composés, et le rapport est alors proche de 7. Quand la détérioration est faible, ces composés deviennent importants par rapport à la dissolution du collagène et le rapport est plus élevé.

Utilisation d'intercepteurs de radicaux libres

Nous avons expérimenté l'hydroquinone et la Tinuvin 292®, une amine à empêchement stérique (HALS), dont l'usage a été développé dans l'industrie pour la protection des vernis et testé dans le domaine de la conservation (6). Ce composé est insoluble dans l'eau, il a donc été utilisé en solution éthanolique et, à titre préventif, avant le traitement au peroxyde d'hydrogène.

Aucun de ces deux composés n'a inhibé la dépolymérisation du collagène. De plus l'hydroquinone présentait l'inconvénient de colorer le parchemin. Nous n'avons pas poursuivi dans la voie des intercepteurs de radicaux libres et, de tous ces essais, nous avons retenu uniquement l'EDTA pour poursuivre notre expérimentation.

Nettoyage des taches sur un système d'aspiration

Afin d'approcher des conditions réelles de restauration, l'expérience suivante a été menée en traitant nos échantillons sur un système d'aspiration à l'aide d'une trompe à vide et en plaçant le parchemin sur un filtre en verre fritté.

Les solutions (environ 230 ml par gramme de parchemin) ont traversé le matériau comme suit:

- 1—EDTA (solution à 2.10^{-3} mole/litre)
- 2—EDTA + H₂O₂ (5 % d'H₂O₂ dans une solution d'EDTA à la même concentration que la solution 1).

L'opération entière a duré deux heures, mais ce temps est seulement indicatif, il dépend bien entendu de la surface à traiter, de la nature de la tache, de la qualité du parchemin, en particulier son épaisseur, et de la pompe qui détermine la vitesse de passage des solutions à travers le matériau. Nous avons observé des détériorations beaucoup moins importantes qu'en immergeant le parchemin dans des bains comme l'indique le tableau III.

Tableau III. Traitement sur système d'aspiration.

Parchemin protégé durée du traitement: 2 h			Parchemin non protégé durée du traitement: 2 h		
	ΔM	N ₂ sol		ΔM	N ₂ sol
1. EDTA	1,8%	<0,1%	Pas d'EDTA	5,7%	0,5%
2. H ₂ O ₂ + EDTA			H ₂ O ₂ seul		

Au vu de ces premiers essais, nous pouvons considérer comme possible l'utilisation de l'EDTA pour protéger le parchemin de la détérioration durant le blanchiment au peroxyde d'hydrogène si des ions métalliques sont présents. Mais à ce point de notre étude, notre préoccupation est double:

- nos analyses sont-elles assez sensibles?
- le traitement peut-il initier un processus de détérioration qui serait trop faible pour être détecté sur le moment mais qui, mettant en jeu des réactions radicalaires, pourrait se propager en s'amplifiant et produire une détérioration au cours du temps?

Vieillessement artificiel

Afin d'accélérer un tel phénomène potentiel, nous avons entrepris un vieillissement artificiel par la lumière.

Tableau IV. Vieillessement à la lumière d'échantillons traités.

	1er groupe		2ème groupe		3ème groupe	
A. 19 jours, 10% HR, 50°C	oui					
B. 20 jours, 50% HR, 30°C	oui		oui			
C. 12 jours, 95% HR, 20-40°C	oui		oui		oui	
D. 4 jours, 95% HR, 40°C	oui		oui		oui	
Éclairement	55 jours		36 jours		16 jours	
Δt à la fin du vieillessement en °C	Tm	-12	Tm	-6	Tm	0
	Tm Cu	-10	Tm Cu	-5	Tm Cu	0
	bain	-20	aspi	-20	bain	-6
					aspi	-6

Les échantillons suivants ont été exposés sous une lampe au xénon à différentes conditions de température et d'humidité:

- 1—parchemin non traité (Tm)
- 2—parchemin + Cu fixé (Tm Cu)
- 3—parchemin + Cu fixé, traité EDTA + H₂O₂ en bain (bain)
- 4—parchemin + Cu fixé, traité EDTA + H₂O₂ par aspiration (aspi)

Ils ont été classés en trois groupes selon la durée d'irradiation. Le premier, constitué des échantillons 1, 2 et 3 a été soumis aux vieillissements A + B + C + D. Le deuxième groupe, échantillons 1, 2 et 4, a reçu les vieillissements B + C + D. Enfin le troisième groupe, comprenant les échantillons 1, 2, 3 et 4 a reçu seulement C + D.

Après un éclaircissement suffisant, les échantillons traités par EDTA + H₂O₂ ont révélé des abaissements de leur température de dénaturation (Td) plus importants que les échantillons témoins non traités, et particulièrement le second groupe, comme le montre le tableau IV. Ceci pourrait être dû à des réactions initiées au moment du blanchiment et amplifiées par l'irradiation.

Conclusion

L'EDTA est une voie possible pour inhiber la détérioration du parchemin lors de l'élimination des taches à l'aide de peroxyde d'hydrogène, si des ions métalliques sont présents.

Les premiers résultats obtenus après vieillissement artificiel à la lumière montrent que des échantillons de parchemin (contenant du cuivre), blanchis au peroxyde d'hydrogène après traitement à l'EDTA, subissent un abaissement de leur température de dénaturation supérieur à celui d'échantillons références vieillis dans les mêmes conditions. Cette modification de la stabilité hydrothermique pourrait indiquer qu'une détérioration a été initiée au moment du blanchiment et qu'elle s'est accentuée sous l'influence du vieillissement.

Ces premiers résultats doivent bien entendu être vérifiés et à cette fin, nous avons entrepris une expérimentation sur un échantillonnage plus vaste. Celui-ci nous permettra d'effectuer d'autres analyses, incluant la mesure des propriétés mécaniques et l'analyse des acides aminés, et ainsi de mieux évaluer la détérioration durant le vieillissement.

Si cette détérioration est vérifiée, nous recommanderons de proscrire l'usage du peroxyde d'hydrogène pour le nettoyage du parchemin.

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Matériaux

Chloramine T : sel de sodium de la N-chloro p-toluènesulfonamide.

EDTA: acide éthylènediaminetétracétique, sel disodique.

Irganox MD 1024®: Bis (3,5-di-terbutyl 4-hydroxy hydrocinnamide). Ciba-Geigy.

Tinuvin 292®: Bis (1,2,2,6,6-pentaméthyl 4-piperidyl) sebacate. Ciba-Geigy.

Abstract

A new and promising deacidification method to prevent the deterioration of acidic papers in libraries and archives has been developed in Germany. The improved liquid-phase process developed by the Battelle Institute is based on a new, non-polluting solvent replacing the environmentally harmful CFCs that are used by other processes. A new neutralization agent containing magnesium titanium ethoxides has been developed to deacidify and partially strengthen the paper. The new treatment solution contains no alcohol co-solvents, and thus undesirable side effects on difficult materials are reduced considerably. Based on the new process, a large scale deacidification plant is being built at the Book Preservation Center of Die Deutsche Bibliothek in Leipzig.

Keywords

Paper deterioration, paper preservation, mass deacidification, Die Deutsche Bibliothek, German deacidification process, microwave drying, new solvents

The German Mass Deacidification Process: Recent Developments and the Realization at Die Deutsche Bibliothek

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Introduction

In the last two decades, various methods have been proposed to protect papers and books against acid-catalyzed deterioration. The common approach is based on the use of deacidification and alkaline buffering. To preserve large quantities of paper-based library materials, large scale deacidification processes had to be developed. Two main principles were established for bulk chemical neutralization: the vapor-phase DEZ process of the United States Library of Congress, and the liquid-phase treatments using magnesium alkoxides or magnesium glycolates in nonaqueous solvents. Since 1980, when a first pilot plant of the "Wei T'o process" was put into operation at the National Archives of Canada, at least three more test facilities were developed in the United States and Europe. The experimental results which are available thus far prove that the methods are effective, and that in principle they achieve what is expected of them (1, 2).

However, there were still some important improvements to be made. The organic CFC solvents (chlorofluorohydrocarbons such as R-12 or R-113) used in nonaqueous liquid-phase deacidification, have become a major concern in discussions of environmental compatibility. It has become evident that the high emissions of solvent vapors from incompletely dried books—or even the use of CFCs—would be banned in future. Other problems have been caused by the additional alcohols required as co-solvents for the neutralizing agents in most liquid-phase processes. Depending on the type of treated materials, undesirable side effects on colours, inks, bindings, glues, and plastics may occur and affect the treatment quality.

Mass deacidification in Germany

In Germany, a research programme on mass deacidification was established at the Deutsche Bibliothek in 1987. The programme is supported by the Federal Ministry of Research and Technology. In cooperation with the Battelle Institute in Frankfurt, (responsible for the scientific and technical work), an initial general evaluation of the existing processes was carried out (3). Based on that state-of-the-art study, it was decided to concentrate on a project to improve the liquid-phase processes.

Efforts were focused on eliminating the weak points of the existing methods in order to realise a mature, readily useful mass deacidification method. As a result, the first German pilot plant was put into operation at Battelle in 1991 (See fig. 1). The main features of the German concept are highly efficient microwave/vacuum drying, a closed solvent cycle with a multi-stage exhaust air treatment, a compact plant design, and a fully automatic process control. The German paper deacidification process is, therefore, non-polluting, easy to operate, and very fast. The pilot plant is designed for a capacity of about 80 books per batch (4).

In the beginning, the chemical treatment was mainly based on the use of magnesium methyl (methoxy) carbonate (MMC) as originally applied in the Wei T'o process. The methanol content of the original solution, that which is mainly responsible for negative side effects, was already partially replaced by ethanol following the example of the French deacidification plant in Sablé. Thus, the active compound became a magnesium-methyl-ethyl-carbonate. However, the treatment was still called a MMC process. Regarding the required solvent, the further use of common CFC solvents was justified by the highly efficient solvent recovery system which achieves a recovery rate of more than 99.5%.

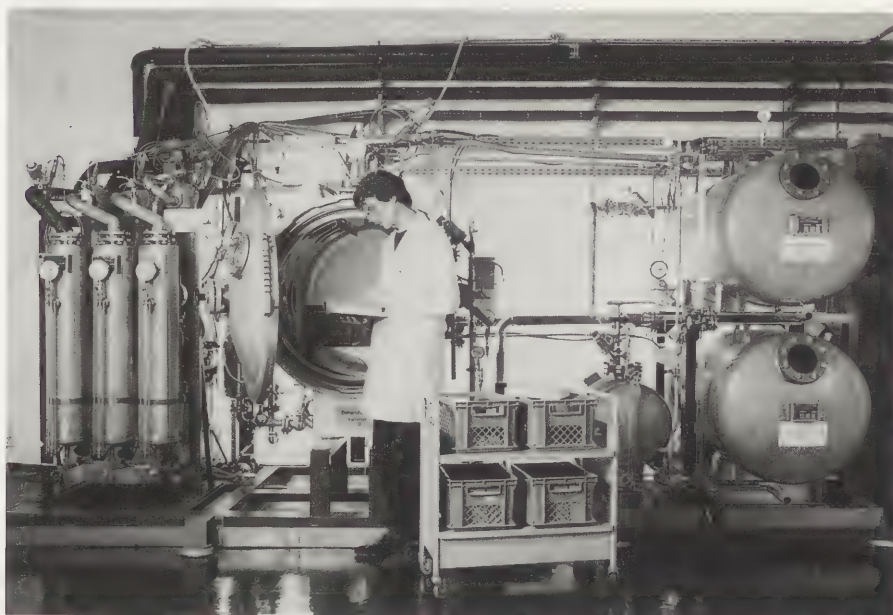


Figure 1. The German pilot plant for liquid-phase mass deacidification, located at the Battelle Institut e.V., Frankfurt/Main.

A new solvent

While the German process has performed satisfactorily in the pilot plant, a considerable part of the research at Battelle was focused on the development of new non-polluting solvents. In most technical areas, there is a great demand for CFC substitutes, and some research efforts have already led to suitable alternative solvents. In many industrial applications, for example, aqueous solutions, hydrocarbons, fluorohydrocarbons, natural plant oils, and other materials can be used instead of CFCs. Nevertheless, a transfer to the field of paper deacidification is hardly possible due to its very high requirements.

By intensive screening and investigation of a great number of different substances, the researchers at Battelle developed a suitable solvent. The new substance is a non-polluting, non-toxic silicon-organic compound with a boiling point at 100°C, called HMDO. Colourless and highly inert, the substance evaporates easily and leaves no odour in the papers. Its excellent properties meet the very specific requirements of a mass deacidification process. The technical design of a plant has to be adapted slightly because HMDO is inflammable like most of the common solvents, with the exception of CFCs.

New agents in paper deacidification

Unfortunately, liquid-phase deacidification methods often have some undesired side effects on treated materials. Some bleeding of printing inks and colours, as well as damage of glues and plastic covers, could be possible, mainly due to the alcohol co-solvents.

The attempt to find new alternative neutralization agents without negative effects has led to considerable research and development at Battelle during the last two years. As a result of intensive searching and laboratory work, a new magnesium-based chemical was found to replace the former MMC. The new agent is a magnesium-titanium-ethoxide called METE. It mixes easily with the HMDO solvent. The new deacidification solution contains no alcohol and thus completely eliminates the known negative effects.

The magnesium compound neutralizes the acids and forms an alkaline reserve against future acid attack. The alkaline reserve is partly dependent on the residual moisture in the paper, but excess METE is hydrolyzed later when the paper takes up moisture again. Besides the deacidification, the METE solution also shows some strengthening effects on brittle paper, due to the effects of titaniummethoxide, known for its reactive properties with hydroxygroups of cellulose forming micro-crosslinkages.

Process description

The deacidification process is still similar to the original MMC method. At the Battelle plant, the time-consuming predrying steps of the other processes (up to two days or more) are reduced by an efficient combination of vacuum drying and microwave heating. During drying, the temperature of the books and papers is constantly monitored and computer-controlled to a moderate level of 50–60°C.

When predrying is completed, the chamber is filled with the deacidifying solution. The books are vacuum-impregnated for a few minutes. The excess solution is then pumped off. Subsequently, the books are dried again by the combined vacuum-microwave drying that is particularly effective in this case. The solvents are completely removed from the paper in less than one hour. No harmful residues are left to be exhaled by the books. The solvent vapors are recovered by condensation and reused to make a fresh solution.

The three step deacidification treatment only takes a total cycle time of approximately two hours, including pre-drying, liquid-phase impregnation, and solvent removal with final drying.

Chemical and physical results

The chemical efficiency and the quality of the deacidification treatment's regularity was demonstrated by chemical analyses of the papers. The results achieved by the treatment with METE are very similar to those found for the former MMC-agents. In figures 2 and 3, the chemical properties of three different titles with different papers are shown. The original pH value of 6.1–4.8 is increased to about 8.8–9.1 (See fig. 2). The alkaline reserve achieved in the paper is in the range of 1.2–2.2% w/w equivalent of magnesium carbonate (See fig. 3). This range of alkaline reserve was achieved due to the different density and porosity of the papers, and also depends on the original acid content. However, no significant differences could be detected in pH value and alkaline reserve on the outer edges of a book, the middle portions, and whole pages.

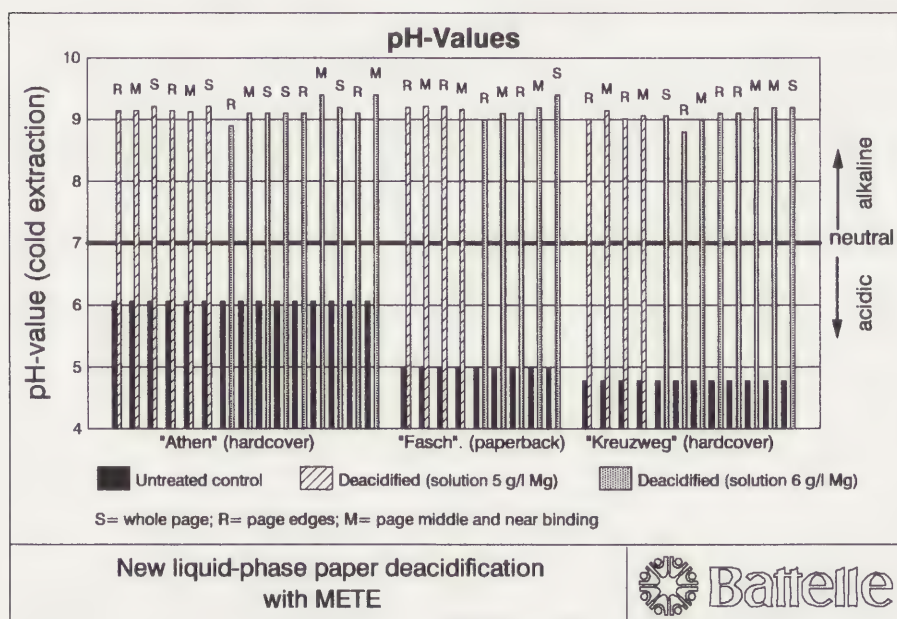


Figure 2. Results of the new paper deacidification process with METE (magnesium-titanium-ethoxide) on treated books. The pH values of various samples (cold extraction) are shown.

A German center for mass deacidification

Based on the new Battelle process, the next step towards a practical use of mass deacidification in Germany was taken. The first large scale deacidification plant is currently being built on behalf of Die Deutsche Bibliothek. This plant is designed and constructed by Battelle. Because of its value as a demonstration

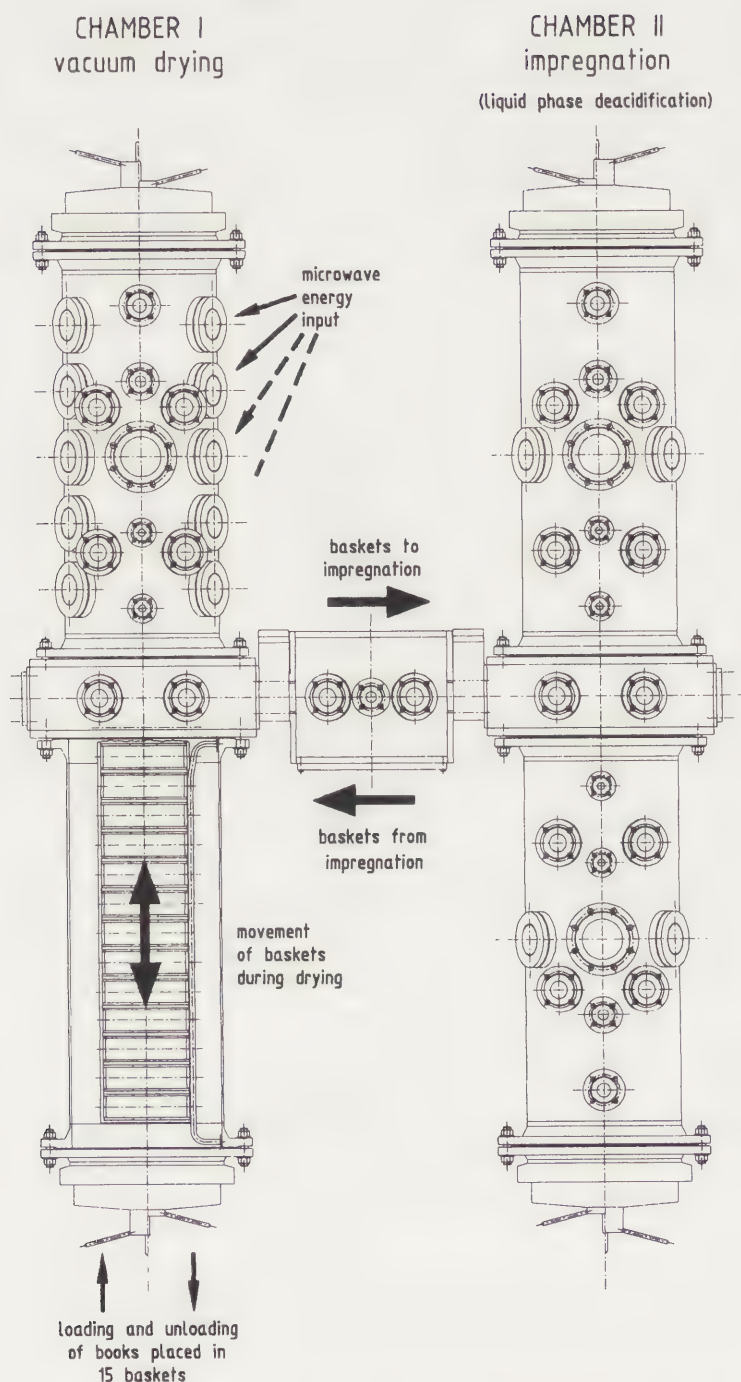


Figure 5. Design concept of treatment chambers for mass deacidification with separate drying and impregnation.

and at last returned to chamber 1 for drying. The whole process is automatically run by computer control, with temperature monitoring is performed by fibre-optical and infrared sensors and a sophisticated control system.

The new demonstration plant is currently under construction at Battelle in Frankfurt. Following the start up of the deacidification process there will be some months of large-scale testing, quality control, and training of staff. The transfer to Leipzig is scheduled for the end of the year. The design of the deacidification plant in Leipzig is shown in Figure 6.

The next stages

The cooperation of Die Deutsche Bibliothek and Battelle on mass deacidification will be continued. The operation of the demonstration plant at the Leipzig Conservation Center will be accompanied by Battelle with scientific and engineering advice. Furthermore, research and development on existing or new promising deacidification methods continue. The combination of technologies

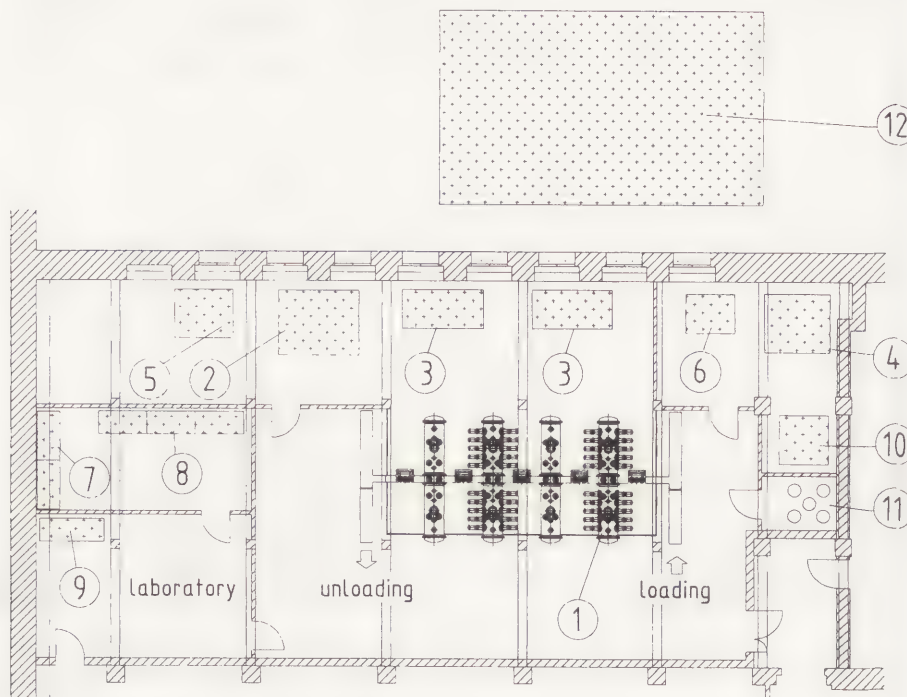


Figure 6. The demonstration plant for paper deacidification as designed for Die Deutsche Bibliothek in Leipzig. The location of the components (final size with 4 chambers and maximum capacity) are shown.

Total area: 12 × 25 m (low ceiling height of basement only 2.4 m)

Legend: 1. Treatment chambers (from right): predrying, impregnation, secondary drying (solvents), post-conditioning; 2. Vacuum pumps for solvent drying; 3. Buffer tank; 4. Cooling machines; 5. Solvent recovery; 6. Vacuum pump for predrying; 7, 8. Electrical supply; 9. Process control; 10. Compressed air system; 11. Nitrogen supply; 12. Solution tanks.

including paper strengthening will be an important future item. The pilot plant will be used for additional trials and experimentation to reach an optimum treatment process and plant design.

Conclusions

The liquid-phase deacidification process developed by the Battelle Institute in Germany is based on a new non-polluting solvent replacing the environmentally harmful CFCs. Furthermore, a new neutralization agent containing magnesium-titanium-ethoxides has been developed to deacidify and partly strengthen the paper. The new treatment solution does not contain any alcohol co-solvents, and undesired side effects on difficult materials are, therefore, considerably reduced.

The Battelle process offers a promising new chance to preserve acidic papers in libraries and archives from deterioration. Based on the new process, a large-scale deacidification plant is being built at the Book Preservation Center of the Die Deutsche Bibliothek in Leipzig.

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Abstract

Manuscript samples with iron gall inks were analysed by gas chromatography-mass spectrometry (GC-MS) and scanning electron microscopy energy dispersive X-ray microanalysis (SEM-EDX). The samples, on paper and parchment bases, showed different colour and acidic behaviour. Inorganic elements analysed by SEM-EDX showed different sulphur and iron distributions on the base. The different ratio between the sulphur and the calcium was noted also. Gallic acid and sugars in the ink were tested by GC-MS. These compounds were identified by mass spectral analysis and co-injection of standard products. The results were different for light inks and dark or acidic inks. The gallic acid remains only in the dark inks, but in the light and very acidic inks, gallic acid could not be found. Sugars that come from gum arabic were present in the light inks and in those dark inks that were not very acidic. The carbonized samples retain very small amounts of sugars.

Keywords

Iron gall inks, scanning electron microscopy-energy dispersive X-ray microanalysis (SEM-EDX), gas chromatography, mass spectrometry, gas chromatography-mass spectrometry (GC-MS)

Table I. pH changes in adding gallic acid when $[\text{FeSO}_4] = 16 \text{ mg/ml}$.

mol GA/mol FeSO_4		pH in adding 16 mg/ml of gum arabic
	pH	
0.036	2.75	3.21
0.369	2.33	2.6
0.923	2.16	2.4
1.847	2.07	2.3

Table II. pH changes in adding different amounts of iron sulphate. [Gallic acid] = 0.04 mg/ml .

mol GA/mol FeSO_4		pH
$1.477 \cdot 10^{-1}$		3.36
$1.477 \cdot 10^{-2}$		3.04
$3.694 \cdot 10^{-3}$		2.65
$1.477 \cdot 10^{-3}$		2.46
$4.950 \cdot 10^{-4}$		2.27
$2.462 \cdot 10^{-4}$		2.19

Organic and Inorganic Components of Iron Gall Inks

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Introduction

For several centuries, iron gall ink has been used to write manuscript documents. We have many bibliographic reports about ink formulae where we can find not only their essential components but also how they are prepared; the addition of other substances to improve the ink quality is noted as well. In iron gall inks, the most important components are the organic extracts of tannins and the gum arabic. The inorganic components are the iron and copper sulphates.

Several recipes from the 15th to 19th centuries have been published in Catalonia, Balear Islands, and Valencia, Spain, and in all of the recipes we find the components noted above (1). Their preparation is based on tannin extraction, with which the iron that yields the iron sulphate forms a black suspension that is retained and thickened by the gum arabic.

One of the most important causes of degradation in ancient manuscripts is the ink acidity. The relationship between the important corrosion that some inks provoke in the support and the fact that a strong black colouring remains in the ink has often been demonstrated. By contrast, no acidity is shown in light coloured or slightly dark inks.

We tried to explain the acidic behaviour and permanence of black colour in some inks. In order to do this, we used gas chromatography-mass spectrometry (GC-MS) to analyse their organic components. The same samples were used in scanning electron microscopy energy dispersive x-ray microanalysis (SEM-EDX) to check the inorganic samples.

Laboratory inks and their behaviour

Inks were prepared in two groups. For the first set, we prepared several different iron gall inks with different amounts of gallic acid while keeping the amount of iron sulphate the same. The second set was prepared so that the sulphate changed and the gallic acid was always the same. The amounts of and ratio between the iron sulphate and gallic acid used to prepare laboratory inks were selected based on the ink recipes. Most of these recipes delineate specific components and amounts, and explain the process of extracting tannins, so that it is possible to deduce that the amount of gallic acid depends on the extraction procedures. In some of them, we added some quantity of gum arabic.

The factors studied in this first step of our work were the pH variation for the inks and their appearance and colouring at the time of preparation and then three months later.

The first group of inks was prepared with invariable quantities of iron sulphate and gum arabic (16 mg/ml of each), while the gallic acid changed (See table I). All of these inks showed a dark colouring and kept it after three months. It was from these samples that we tested the chromatographic analysis.

The following step was to check that the pH changes together with the increase of iron sulphate, whereas gallic acid concentration remains constant and low, equal to 0.04 mg/ml (See table II). At the same time another group of inks was prepared; in this case, iron sulphate was the substance kept constant (equal to 0.4 mg/ml) while the gallic acid changed (See table III).

Fifteen days later, all of the inks related to Table II were the colour of iron

Table III. pH changes in adding different amounts of gallic acid. $[\text{FeSO}_4] = 0.4 \text{ mg/ml}$.

mol GA/mol FeSO_4	pH
0.184	3.68
0.923	3.47
3.694	3.34
9.235	3.00
18.471	2.84

Table IV. pH changes in adding different amounts of iron sulphate. $[\text{GA}] = 5 \text{ mg/ml}$.

mol GA/mol FeSO_4	pH
18.471	2.92
1.847	2.76
0.461	2.39
0.184	2.16
0.061	2.00
0.030	1.96

oxides, similar to the light inks. At a concentration of approximately 16 mg FeSO_4/ml , an important sediment of iron sulphate and iron oxides was noticed. Only the first sample with 0.4 mg/ml of iron sulphate concentration and 0.04 mg/ml of gallic acid kept the relatively dark colouring, however, the ink was very clear. The inks in Table III remained dark and they were darker when the amount of gallic acid was greater.

Another group of inks was prepared (See table IV). In this case, 5 mg/ml of gallic acid solution was used prior to different amounts of iron sulphate. These inks had 125 times more gallic acid than those shown in Table II. All of them were dark and dense and their acidity increased together with the amount of iron sulphate added.

All of these tests led us to the following conclusions: first, the pH of the ink is always acidic and the acidity increases with the amount of gallic acid if it is enough; as iron sulphate is added, it reacts with a greater amount of gallic acid, so the ink becomes darker, more compact and more acidic. Secondly, the degree of acidity of the inks and the variation of the concentration of their components suggest that the acidic group takes part in the ink formation. This is implied because it is unlikely that the complex only has stability with the hydroxyl groups when the pH remains below 3. Finally, when gum arabic is added to the ink, the pH becomes less acidic.

The analysis and the samples

We divided our work into two parts. First, we analysed the inorganic components by SEM-EDX and then we used GC-MS to identify gallic acid and sugars.

All of the eleven samples tested were obtained from the "Arxiu de la Corona d'Aragó." They were not very valuable, but they were chosen for their different appearances and acidity levels. Two of the samples were on parchment, a 16th century sample with light ink and a 17th century sample with dark ink. Another seven samples were on paper. Of the three samples with light ink, two were from the mid-16th century and the third from 1757. The other four samples with dark ink dated from the end of the 16th century to the beginning of the 17th century. Three of these four latter samples had slight acidity problems. Another two samples had a carbonized paper base.

Scanning electron microscopy and X-ray microanalysis

The first step in this work was to analyse inorganic components. A previous study was published by Sistach (2). In our study, two kinds of samples were prepared for each kind of ink; one was imbedded in Spurr resin and the other was prepared without resin (3). We can check the inorganic elements and their distribution on the base. Specific areas with ink, bordering or around the ink can be analysed on the surface as well as into the paper base. The following inks were analysed: (A) light ink, (B) the dark but not black ink, (C) the black but not acidic ink, and (D) the very acidic ink.

We checked the penetration of the ink into the paper and the parchment. It is higher when the base is paper. Similarly, when we looked at the paper surface, we noticed particles between fibres and found them to be precipitated CaSO_4 (See fig. 1).

SEM-EDX analysis of light ink (A) and dark-black inks without acidic behaviour (B, C)

The areas with ink often show calcium, iron, and sulphur, and sometimes aluminium and potassium. The acidity depends on the ratio between the first three elements noted above (Ca, S, and Fe) when analysing areas that contain ink or are next to it, compared with other areas far away. The inks with light colour (A) have the ratio $\text{S/Fe} < 1$ in superficial areas with ink (See fig. 2). When the ink is dark but not acidic (B,C), the ratio S/Fe can be greater than or equal to 1.

Another important factor determining ink behaviour is the presence of calcium, because in light and dark non-acidic inks, this element keeps their ratio of Ca/S

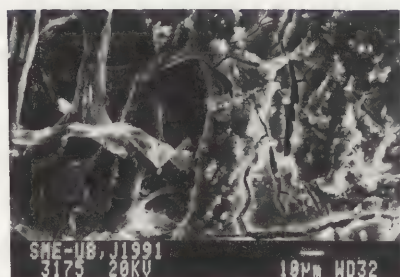


Figure 1. SEM image for a bordering area with and without ink on a paper base. We can see particles of CaSO_4 on and between the fibres.

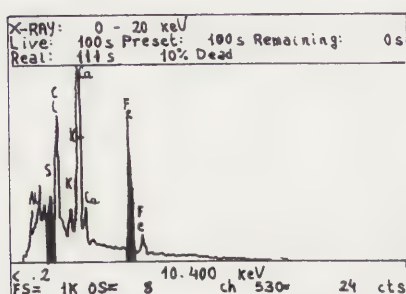


Figure 2. Spectrum of light ink on a paper base in a specific area with ink.

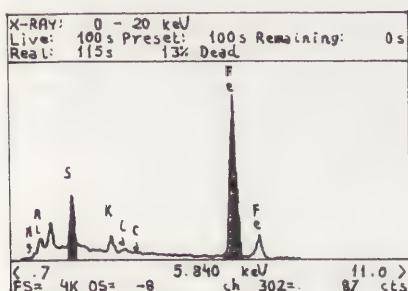


Figure 3. Spectrum of acidic ink in a specific area with ink on a paper base.

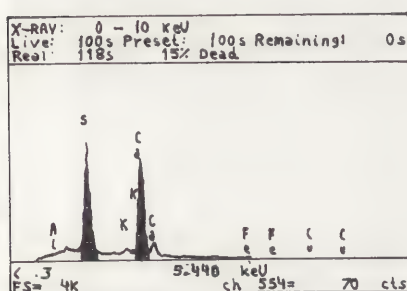


Figure 4. Spectrum of acidic ink in a zone 3 mm around the ink on a paper base.

greater than or equal to that of areas on the surface and into the support, although the iron is not present. For very dark inks on a parchment support, the ratio is $S/Fe > 1$ and $S/Ca \geq 1$ in inner areas with ink. This one should be acidic if the support was paper.

SEM-EDX analysis of inks with corrosive behaviour (D)

Most of the areas with ink that were analysed showed a ratio of $S/Fe < 1$ (See fig. 3). The reason for finding less sulphur than iron in these particular ink areas for acidic samples is probably because the sulphur that comes from the sulphuric acid migrates to the surface and to the inner zones far away from the ink when paper carbonization is important. This is supposed to happen because in areas next to the ink we found significant quantities of sulphur together with calcium, but in this case the ratio S/Ca can be greater than one (See fig. 4). So we can compare the sulphur excess in contrast with the alkaline reserve of the paper. Similarly, we have noted a great amount of potassium in some samples with acidic ink (4).

The presence of significant amounts of iron in acidic inks can contribute to cellulose degradation also, but if we quantify the acidity that comes from the sulphuric acid with that which comes from iron, we should infer that it is mostly due to the sulphuric acid (5).

Analysis by GC-MS

The second part of our work was directed at the analysis of organic components. Our main aim was to check whether or not gallic acid remains in the ink. In order to investigate this important point, we worked in three steps:

1. We prepared several iron gall inks with different quantities of gallic acid. These are represented in Table I.
2. We investigated the technical effectiveness in order to determine whether or not the gallic acid remains in inks previously prepared at the laboratory. The relationship between the quantity of gallic acid used to prepare the inks and the quantity found was confirmed.
3. Finally, we tried these established conditions on original samples from the "Arxiu de la Corona d'Aragó." They were the same samples tested with SEM-EDX.

Method

In order to ensure good conditions for the identification of gallic acid in the laboratory inks, we took several steps: a) hydrolysis of the ink (25 μ l of ink + 100 μ l HCl 3%) for 2 hours at 105°C; b) extraction of the organic components with ethyl acetate and passing of the extract through a Na_2SO_4 anhydrous column; c) drying of the extract with a rotary evaporator in order to ensure that no water remains in the sample; and d) silylation of the dried samples using two different reagents (acetonitrile 50 μ l:BSTFA 50 μ l:triethylamin 25 μ l and pyridine 100 μ l:BSTFA 50 μ l:trimethylchlorosilane 2 μ l) (6).

In order to analyse original ancient inks, we had to remove them from the support; the process was made mechanically and some parchment and paper fibres can be removed together with the ink. The ink samples (2–5 mg) were hydrolysed with 100–200 μ l of HCl 3% at 105°C for 2 hours. We worked also with paper and parchment samples soaked in hydrochloric acid to directly yield the hydrolysed components.

The same four kinds of samples were analysed: (A), (B), (C), and (D). For each ink test, another sample spiked with standard gallic acid solution was prepared and compared with this standard solution.

The working conditions for GC were as follows: A KONIK KNK-3000 HRGC (FID detector) equipped with a DB-5 column (J & W Scientific, Folsom, CA, USA) 25 m \times 0.22 mm, 0.25 μ m film. The carrier gas was H_2 (12 psi) and nitrogen was used as the make up gas (30 ml/min). The mode injection was Split 1/20. The temperature was initially 60°C for 3 minutes, then programmed at 6°C/min to 285°C.

The working conditions for GC/MS were as follows: A KONIK 3000 gas chromatograph was used, coupled with a magnetic mass spectrometer "VG TS-250" (Fisons Instruments, Manchester, UK) and VG 11/250 data system. The GC conditions were the same noted above and the column was coupled to the ion source. Helium was the carrier gas. The mode of ionization was electron impact and the conditions were as follows: ionization energy 70 eV, mass range 45–500 amu, scan time 2 sec/dec, resolution 500.

Results

The results varied according to the characteristics of the ink. The light inks (A) and the very acidic inks (D) did not have any gallic acid remaining. However, the (B) and (C) inks retain small quantities of acid (See fig. 5). We can see in Figure 5 how light and non-acidic inks contain some sugars (galactose, rhamnose, and arabinose). However, the very acidic inks retain few organic substances. These compounds could have disappeared because of acidity. The chromatograph provides information about gallic acid in relation to the standard solution. Mass spectrometry allowed us to identify this substance in a specific m/z 281, 458 (See fig. 6).

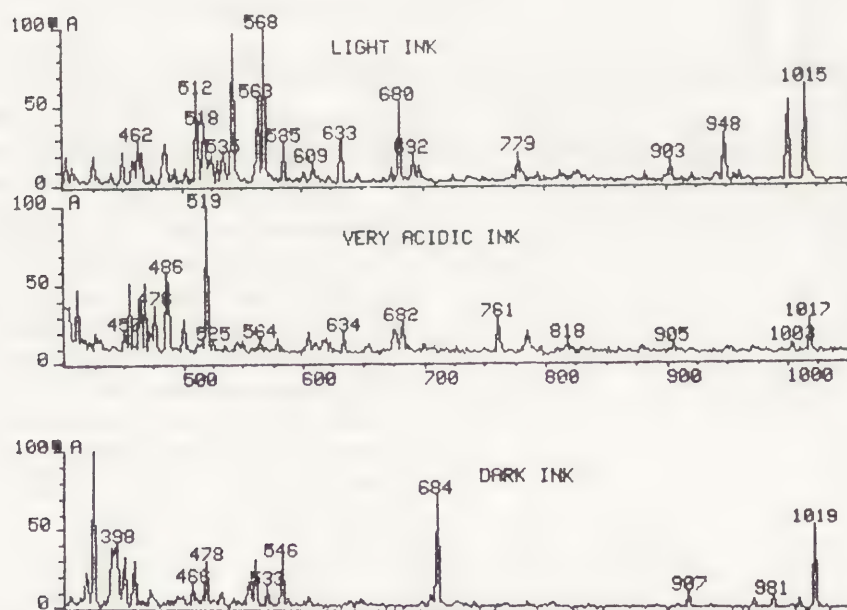


Figure 5. Chromatogram of three different kinds of ink: light, very acidic, and dark ink. The dark ink retains gallic acid at 981 scan.

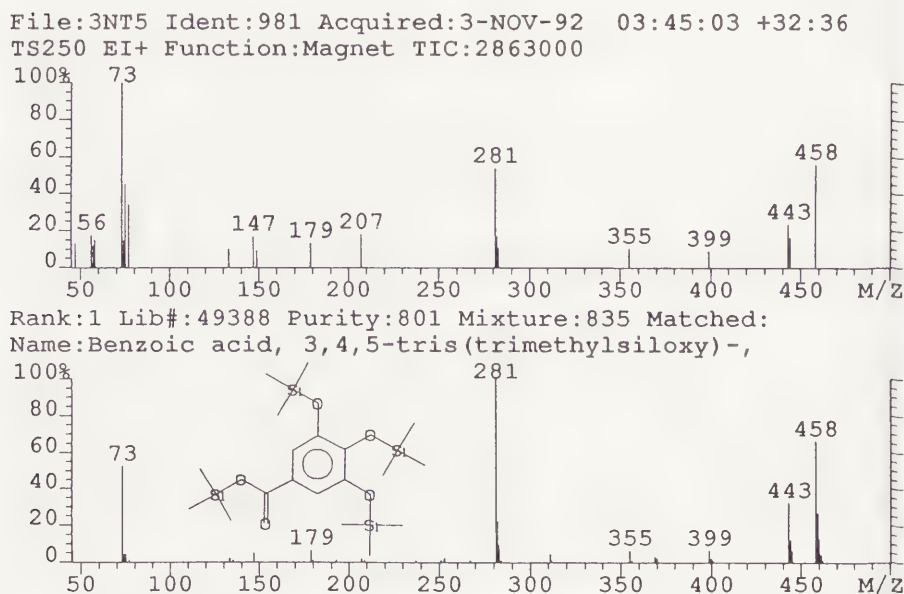


Figure 6. EI Mass spectrum of gallic acid TMS derivative.

Conclusions

The pH variations obtained from different inks made with iron sulphate and gallic acid in variable ratios seem to indicate that the acid group of gallic acid contributes to the complex formation of the ink. As far as a saturated solution of iron sulphate is concerned, the ink will be darker and more dense as gallic acid increases. Similarly, we determined the pH of ink increases as gum arabic is added.

SEM-EDX tests of ancient inks indicate the following conclusions. The Ca ratio in paper related to S and Fe in ink is very important in order to counteract acidity coming from sulphuric acid. Distribution and ratio of these three elements in the support changes according to ink acidity; therefore, in very acidic inks, the S from sulphuric is present in great amounts if we compare this element with Ca in areas around the ink. However, we do not find significant amounts of S in ink zones because S moves toward to the areas that border the ink, although we do find some iron in ink zones.

Analysis of the organic compounds in the ink by GC-MS indicate the following conclusions: It seems that the fact that light inks are found is due to the scarce quantity of gallic acid used in ink preparation, as this acid could disappear with the passage of time. The dark colour of ink that bears no trace of acidity is due to gallic acid remaining in the ink. The fact that black colour is found in very acidic inks that carbonized the base is not because ink retains more gallic acid but because when the organic compounds and the base carbonize, black colour appears.

It is the particular ratio of the three compounds gallic acid, iron sulphate, and gum arabic that determines ink quality and justifies its later acidic behaviour.

Acknowledgements

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4. Conditions in microanalysis: Beam current 0.8×10^{-9} A; accelerating voltage 20 Kv; 100.000 magnification; working distance 33 mm; Model JSM 840 (Jeol Ltd.) electron microscope with scanner AN 10000 (LINK SYSTEMS) and Be window.
5. G. Banik, H. Stachelberger, and K. Messner, "Untersuchung der destruktiven Wirkung von Tinten auf Schrifttrgermaterialien," *Restaurio* 4 (1988): 302-308.
6. Acetonitrile MERCK; BSTFA Bis (Trimethylsilyl trifluoroaceta-mid) MERCK; Triethylamin MERCK; Pyridine MERCK; Trimethyl-chlorosilane RPE CARLO ERBA; Ethyl acetate MERCK; sodium sulphate anhydrous RPE CARLO ERBA; Fe SO₄.

7H₂O PANREAC; Gallic Acid MERCK; Arabic gum PANREAC; Methanol MERCK; Water MILLIPORE; Hydrochloric acid MERCK.

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Abstract

Pigment-coated papers have been used, virtually since the beginning of papermaking history, for their special properties. These properties, however, may render coated papers more susceptible to certain types of damage and more reactive to certain conservation treatments. This article, the first of two, provides a chronology of the history and use of coating materials and techniques, with an emphasis on the roles that pigment properties play in influencing the final coating properties. Some common pigments used for paper coatings are listed, along with their elemental compositions and properties such as particle size, refractive index, brightness, and pH. The influences of various binders (protein, starch, resin and synthetics), additives (eveners, dispersing agents, anti- and defoamers), and finishing techniques (supercalendering) on coating properties are also outlined. U.S. grading standards for modern pigment-coated papers, based on rawstock, brightness (single wavelength reflectance), and gloss (75° angle), are listed to aid in the characterization of unknown papers.

Keywords

Coated paper, pigment-coated paper, clay-coated paper, color-coated paper, prepared paper, prepared-ground paper, enamel paper, surface-sized paper, hand-coated paper, brush-coated paper, machine-coated paper, off-machine coated paper, brightness, gloss, technology, history, treatment

Pigment-Coated Papers I: History and Technology

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Introduction

Museums, libraries, and archives contain large collections of pigment-coated papers, which are often the primary support for various drawings and printing processes. These processes are executed on papers having opaque white pigment coatings because of the special properties imparted by such coatings. For instance, pigment-coated papers provide a smooth, white ground for metal point drawings and ink illustrations; an inert ground capable of maintaining registration throughout multiple inkings for chromolithographs or off-set lithography; and a luminous, sharp background for letterpress, relief, intaglio, and photomechanical prints, bookplates, and photographs.

Unfortunately, pigment-coated papers may be more easily marred by scratches, and more retentive of stains and dirt, than uncoated papers [1–9]. This is because pigment-coated papers are produced by modifications to standard papermaking practices with respect to furnish (materials such as rawstock, pigments, binders, and additives) and formation (manufacturing procedures such as calendering) [10–32]. Such modifications are necessary to achieve the specific properties of brightness, gloss, smoothness, opacity, and ink receptivity required, in particular, by the printing trade. The various formulation materials and techniques, and their effects on the properties and use of pigment-coated papers, are the subject of this article, which is the first of two studies on the topic. The special problems posed by pigment-coated papers requiring conservation treatment involving the application of solvents is the subject of a second study reported in these Preprints.

Numerous terms are used to describe pigment-coated papers. Generally, the terms reflect the diversity of materials and techniques used to coat papers. For instance, such papers may be described as coated paper, pigment-coated paper, clay-coated paper, color-coated paper, prepared paper, prepared-ground paper, enamel paper, or surface-sized paper, etc., which may be one-side coated, two-side coated, light weight coated, hand-coated, brush-coated, machine-coated, or off-machine coated, etc. The following review of the literature attempts to define some of these terms and provide a brief historical overview of materials and techniques used in formulations. All dates noted in this section should be interpreted as approximate, since dates may vary depending on reference and geographical sources, or change as new information is discovered by future research.

Formulations: some materials and techniques used up to the mid-20th century

Pigment-coated papers consist of a paper base covered by a mixture containing at least a binder and inert pigment (Table I). The earliest examples may have originated from China, where paper surviving from 450 CE is reported to have a starch sizing and gypsum surface treatment [16]. During the Tang Dynasty (CE 618–907) papers may have been coated with white mineral powders and wax, which filled interstices between fibers in order to increase water repellency and smoothness for fine calligraphy [20]. By the 8th century, Arab cultures had reportedly modified paper with talc, gypsum or chalk, which could also be mixed with rice starch to coat the paper for increased whiteness [10, 12].

During the middle ages, papers were coated with white pigments to provide an appropriate surface for metal-point drawings, executed with a metal stylus made of silver or copper, which before the discovery of graphite represented the only

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Table I. Some typical coating pigments with common names and commercial use, as well as elemental composition and relative properties of refractive index (n), average optimum particle size in microns (μm), brightness (GE percent reflectance at 457 nm), and pH. [Compiled from: Beazley, Casey 1961, Kouris.]

Pigments	Al	Si	K	Ti	Ca	S	Ba	Zn	Pb	n	μm	Bright- ness	pH
Barium sulfate (baryta or blanc fixe) {weight, purity, brightness, finish}	—	—	—	—	—	+	+	—	—	1.64–1.66	0.11–0.54	95–98	3.5
Calcium carbonate (ground or precipitated) {opacity, brightness, dull finish, ink affinity}	—	—	—	—	+	—	—	—	—	1.57–1.66	0.1–10	93–98	7–10
Calcium sulfate (gypsum or pearl white, crown filler, alabastine, etc.)	—	—	—	—	+	+	—	—	—	1.52	0.2		
Calcium sulfite {brightness, absorbency}	—	—	—	—	+	+	—	—	—		6.5	92–96	8–9
Clay (residual or transported, kaolin) {body, finish}	+	+	—/+	(+)	—	—	—	—	—	1.55–1.56	2.0 0.4–5.0	65–91	4.3–7
Diatomaceous silica {dull, abrasive, resistant to blackening}	—	+	—	—	—	—	—	—	—		1.5×10 –50	65–95	5
Lead white (basic lead carbonate, hy- drocerussite)	—	—	—	—	—	—	—	—	+	1.80–2.08			
Satin white (calcium sulfoaluminate) {finish, brightness, gloss}	+	—	—	—	+	+	—	—	—	1.46	1–2 by 0.1– 0.2		
Talc	(+)	+	—	—	(+)	—	—	—	—	1.57	2.0		4–6
Titanium dioxide (rutile or anatase) {opacity, brightness, white- ness, smoothness}	—	—	—	+	—	—	—	—	—	2.5–2.7	0.2–0.5	97–98	4–6
Zinc sulfide	—	—	—	—	—	+	—	+	—	2.37	0.3	94–96	
Lithopone (Orr's White, Charlton White)	—	—	—	—	—	+	+	+	—	1.84–2.00	0.3–0.5		
Zinc oxide (opacity)	—	—	—	—	—	—	—	+	—	2.01–2.03			
Polystyrene	—	—	—	—	—	—	—	—	—	1.59	0.5		

“dry” medium available for very finely detailed drawings [2]. Coated or prepared-ground papers had the additional advantage of being “erasable,” in that media could be scraped and/or burnished away (or coated over) if changes were desired. To prepare such paper, coating material, mixed with approximately two parts water, was poured on and hand-brushed evenly over the paper, which was then loft-dried [23]. Burnishing, usually by hand with agate stone, created different surface effects, such as increasing smoothness by evening out surfaces, saturating color by compressing pigment, and creating luminosity from increased gloss. Early treatises on recipes for prepared papers mention ground bone ash, powdered cuttlebone, or gypsum, mixed with aqueous binders of glue or gum, or with linseed oil [15, 19, 24, 29]. A treatise on Persian paintings reportedly suggests a two-layered ground consisting of plaster, glue and grape treacle topped by lead white and oil varnish [7].

By the 16th century, coatings were applied to the backs of playing cards, to improve strength and durability. By the mid-16th century (1540) hammer-glazing had replaced hand-burnishing [23].

In the mid-18th century (1764), a coating mixture containing lead white, plaster of Paris, lime size, and nut or linseed oil was patented [19]. There is some reported use at this time of zinc white (1775), a very white, bright and opaque pigment [21, 22]. After the turn of the century, in 1827, enamel paper was made with lead white, isinglass, gum, and animal size, several coats of which were applied and then burnished by plating or running the coated paper, in contact with a steel plate, through a press [19, 22]. By 1830, high gloss could also be imparted by burnishing wax and rosin-treated paper with calendering [19].

The early 19th century witnessed the development of several new coating mixtures. The most popular mixture, introduced around 1807, was a combination of casein and animal glue with China Clay or kaolin (hydrated aluminum silicate extracted from feldspar in granite, with traces of muscovite mica and potassium in primary or residual sources, or yellowing titano-ferrous impurities in secondary or transported sources) [12]. Clay coating made paper whiter, heavier and more receptive to ink. The end of the century (1879) marked the introduction of a pigment coating used for the production of high gloss art and off-set printing paper, satin white (from slaked lime treated with paper makers' aluminum sulphate). Satin white has a high pH, enabling it to augment clay, and to be used in binders of gum arabic, casein, soy protein, hydroxyethylated starch, or carboxymethyl cellulose to provide a satin-like gloss following relatively light calendering [21]. It also has a bright color, but since it is expensive, difficult to handle, and has a high adhesive demand, it is used today primarily for off-machine coating of specialty papers [14]. By the end of the 19th century there was an increased use of baryta (specifically precipitated barium sulfate from barite). Barium sulfate itself comes in two forms, either as the natural mineral barite or as the artificial blanc fixe which may be derived from barite or witherite (a barium carbonate ore in England and Europe). Baryta, or blanc fixe, makes a brighter, denser, and less porous coating, used for special grades of chart papers and for photographs, although it is now being replaced in part by titanium dioxide [14, 21]. When barium sulfate is co-precipitated 7:3 with zinc sulfide, the combination forms lithopone, which became a substitute for lead carbonate. Another, lesser used, pigment was calcium carbonate (natural ground chalk and limestone from calcite, or precipitated as aragonite).

The 20th century ushered in several new materials, starting with the introduction in 1906 of titanium dioxide (made from ilmenite, a double oxide of titanium and iron, processed by sulfuric acid or chlorine, and occurring as either anatase or the more opaque rutile). Titanium dioxide is so opaque and white that only a small amount is needed [21]. It may be bulked up by calcined clay or substituted 25-50% by synthetic silicas and silicates [12, 21]. Also used during the early part of the century were binders of rubber latex (1927), peanut and soy proteins (1937), and pigments such as precipitated calcium carbonate (1925), diatomaceous earth (1938), and zinc oxide (1933), used for early photocopying paper. By the middle of the century, fluorescent whitening agents (stilbenes, salicylates, benzophenones, benzotriazoles and others) [3, 21, 26], and acrylic gessos [8] had been developed, and there was more use of talc (hydrated magnesium silicate with hydrophilic, hydrophobic, and oleophilic properties), used to control wax-like pitch from sulphite wood pulp [21]. Resin binders included urea and melamine formaldehyde resins (1946), polyethylene resins (1946), acrylic emulsions (1952), acrylonitrile and polyvinyl alcohols [9], as well as latexes of rubber, butadiene-methacrylate and styrene-butadiene (1947) [21].

The 19th and 20th centuries also fostered the development of new coating application techniques. In the last quarter of the 19th century, as hand-made paper was replaced by machine-made paper, hand-coating and hand-brushing were replaced by automated "off-machine" coating processes. Off-machine coating is carried out separately from the papermaking machine. One of the earliest examples employed a single-surface brush-coating machine (1852) which used a splatter brush to apply to the paper the correct weight of coating material which was then smoothed by a coarse brush, refined by a firm brush, and finished by badger-hair brushes, and festoon-dried [6]. This application technique resulted in poor uniformity of coating when tested by quality-control measurements of

"wet thumb" and "thumb rub" tests [23]. By the late 19th century (1880), double-surface brush-coating processes were developed. Since brush maintenance was time-consuming and expensive, brush-coaters were replaced at the turn of the century by roll-spreading coaters (1920), which quickly and evenly metered and spread coating material on paper using rotating rolls. Roll-coaters worked best with starch adhesives. These early high-speed coaters initiated the eventual mass production of coated papers [13]. Toward the middle of the 20th century air-knife coaters (1940) were developed, which used a stream of air from a transverse nozzle to control both coating weight and spread in one simple operation, by leveling off excess coating to form a smooth surface which was dried in hot air tunnels. Later developments resulted in the flexible or trailing blade-coater (1950), which utilizes a flexible blade running against paper backed by a rubber roll, followed by drying in air cap driers. More recent developments include extrusion coating, whereby thermoplastic polyethylene resin is melted and extruded in a continuous flow under light pressure through a film-forming slot-die; it is then stretched and rapidly combined with paper between a rubber-covered pressure roll and a water cooled chromium plated steel roll to form a lasting bond with the paper [21].

Formulations: some current materials and techniques

Today, pigment-coated papers account for 20% of all paper sold in the United States. At least ten types of coaters have been developed, including dip, brush, knife, roll, air-brush, spray, extruded, print, cast, and strip coaters. Currently, most coated paper is machine-made, meaning that the coating is applied to the paper as part of the papermaking process. Coated paper may be graded in different ways, including by use or by function, such as coated litho grade (water-resistant sized, one-sided coated paper) or coated book grade (suitable for reproducing halftone photomechanical illustrations) [13, 14]. Examples of U.S. paper grade standards for pigment-coated papers are outlined in Table II.

Table II. Examples of grading standards in the U.S., with GE brightness (percent reflectance at 457 nm) and TAPPI gloss (T480 at a 75° angle). [Sources: Casey 1961, 1985.]

Grades	Types	Uses	Rawstock	Bright- ness (GE)	Gloss 75° (separate grading system)
1	Merchants Grade, coated enamel, coated wood- free	multicolor printing, advertis- ing, bro- chures	100% chemical pulp (basis weight g/m ² = 100–150)	85+	45+ (glossy)
2	Merchants Grade, coated enamel, coated wood- free	multicolor printing, advertis- ing, bro- chures	100% chemical pulp (basis weight g/m ² = 75–150)	83–84.9	25–35 (dull)
3	magazines, cata- logs	magazines, catalogs	chemical & me- chanical	79–82.9	25– (matte)
4	coated ground- wood	magazines, catalogs	mechanical & chemical	73–78.9	25– (matte)
5	publication grade, coated ground- wood	magazines, newspa- pers	mechanical	72.9–	25– (matte)

Pigments

Modern coatings are composed not only of pigments and binders, but also additives and fluid (water). Ninety percent of today's pigment-coated papers are clay coated. The size of clay particles varies greatly and affects covering power, brightness, gloss potential, and ink and varnish hold-out. Calcium carbonate is

currently the second most important pigment, and it is used with clay to increase brightness, opacity and ink receptivity. Some pigments have been put to new uses. Amorphous silicas and silicates, such as diatomaceous silica (Kieselguhr or infusorial earth) from the fossil remains of microscopic diatom plants, are used to reduce gloss and increase resistance to "blackening" upon calendering. Luminosity is enhanced by fluorescent pigments having an average size of 1 micron, which improve brightness, or by phosphorescent pigments having an average size of 5-10 microns, which create an afterglow (useful for special map and display papers). Sulfides of zinc or cadmium create a short afterglow, while strontium or calcium create a long afterglow. Finally, modern coatings may contain plastic pigments such as polystyrene, which is widely used in publication-grade coated papers [12, 13, 20].

Binders

Modern coating binders provide bonding strength among the pigment particles and the rawstock. They also act as barriers controlling ink absorption and hold-out, and they influence the rheology (flow), water-holding, and set-time of wet coating. Papers with strong binding adhesion are called "hard-sized" while those with weak binding adhesion are called "soft-sized" [13, 14]. The principal binders in use today are classified as either hydrophilic water-soluble colloids based on starch (corn, tapioca, white potato, sorghum, sweet potato, rice, and wheat) and protein (glue, casein, and soy), or resin or "rubber" latexes and resin emulsions in aqueous medium, such as styrene-butadiene, polyacrylate, and polyvinyl acetate (sometimes used with starch and protein) [13, 14, 21].

Starch, because of its low cost, is the prevalent binder in the U.S. today, although to control its high viscosity and tendency to gel, retrograde, and lose strength, it must be modified by oxidation, chemical treatment (hydroxyethylation), enzyme conversion or conversion to dextrins. Oxidized starch (treated with alkaline sodium hypochlorite) is used primarily for off-machine coatings. Chemically modified starch is used for size-press coatings or trailing blade-coaters because of its high viscosity and ink receptivity. Starch converted by enzymes (inactivated by heating to 205-212 degrees F for 10-20 minutes or by phosphates, silicates, acids, formaldehyde, etc.) is the principal binder for machine-coated publication papers because of its low cost and ease of adjustments. Conversion to dextrin is done by dry-roasting starch at low temperatures for British gum, which is the best dextrin for coatings as compared to canary or white dextrin, produced by high temperatures and acid treatment. Water-resistant starch is required for coated lithographic paper, tag papers, washable wallpaper, fancy wraps, etc. Compared to casein, starch binders can be produced with less foam, odor and spoilage, although the final coating may have lower bonding strength, water resistance, finish and oil absorption.

Animal glue (bone or preferably hide) is presently used only for coated specialty papers such as playing cards, wallpapers, metal-coated papers, and grades needing high gloss and water resistance. Technical grade gelatin is used with barium sulfate for photographs, with glycerol, sorbitol, and butanol added for conditioning. Glue can be hardened for water-resistance with chrome alum or formaldehyde treatment, although it never becomes as resistant as casein. Casein is today used for off-machine coating of very high-grade printing papers and for machine-coating of paper boards. It is made from curd from coagulated skim milk, acid-separated and alkaline treated, which none-the-less retains some fat that may result in the formation of grease spots. It has a high degree of water-resistance if treated with formaldehyde, zinc salt solution, alum acids, or lime. Soybean protein from soy flour is used in washable wallpaper, and as fluid extender in casein coating mixtures, although it is not as readily waterproofed.

Resin latex or emulsion binders are used for both off- and on-machine coating (generally in combination with starch, soybean protein, or casein), to increase stabilization against mechanical breakdown from high shear on roll-coaters; to improve water-holding properties; and to reduce costs. Latexes can plasticize starch coatings for calendering, flexibility, and wet-rub resistance. Synthetic resin latexes and emulsions have good bonding strength, smoothness, flexibility,

dimensional stability, curl resistance, wet-rub resistance, and gloss, and some of these properties even improve with age. Styrene-butadiene latex, which provides a very smooth surface, high finish, and crisp edge when folded, has been used as the sole binder in many modern European and Japanese mills [23]. These resin and latex binders calender easily because of thermoplastic qualities, but they may also "blacken" or darken on calendering.

Other binders used in lesser amounts are polyvinyl alcohols which have high pigment bonding strength but also high cost, and water-soluble cellulose derivatives which have good bonding strength, flexibility and oil resistance, but high viscosity. Other water soluble resins may include polyacrylic acid, polyacrylamide, and polyacrylonitrile.

Additives

Modern additives serve many purposes and may include eveners (levelers and smoothers), pigment-dispersing agents (fluidifiers, stabilizers, softeners, plasticizers, lubricants), and anti- and defoaming agents, etc. [14]. Coatings with starch binders may require leveling agents or soaps such as sodium, ammonium or calcium stearates (which also minimize dusting and increase gloss during calendering); fluidifiers and viscosity stabilizers of urea and dicyandiamide, or polyoxyethylene stearate, polyethylene glycol laurate and sulfated oleic acid (used with enzyme-modified or thermochemically-modified starches); softening agents including invert sugar, sorbitol, urea, glycerine, or corn syrup (to increase pliability); and plasticizers or lubricants such as calcium stearate, resin latexes, ethanolamine soaps, alkyd resins, fatty acid esters, soaps, and polyglycols. Coatings with casein, soy protein, resin latex and resin emulsion binders may generate foam, which can form pinholes and craters as air bubbles burst through the coating upon drying. Foam may be composed of fine bubbles, dispersed throughout the coating mixture, or coarse froth along the top of the mixture. Anti-foamers include sulfonated oils, pine oil, amyl alcohol, skim milk, ether, kerosene, tributyl phosphates, silicones, and other agents which depress surface tension and convert fine foam, which undermines coating weight and structure, into coarse froth expelled from the surface of the coating. Defoamers may be added to coating formulas to lower surface tension if foaming has already begun (0.1–1.0 % total weight of solids; too much can cause problems in printing offset papers) [14]. Latex binders might require stabilizers of anionic and nonionic surfactants such as sodium dodecyl sulfate, polyethylene oxide alkyl, or alkyl/aryl ethers.

Other additives might include smoothing agents, improving flexibility and preventing pinholes, such as pine oil (also a preserving agent) and sulfonated oils (0.1–0.5% total volume of coating mix; too much can cause oil spots). Carboxymethylcellulose can control viscosity and minimize binder migration. Amines increase gloss. Wax emulsions (paraffin or microcrystalline) decrease dusting during calendering, and increase water repellency, flexibility and gloss. Carnauba wax may be used with friction calendering for high gloss. Shellac dispersed in ammonia has been used in paper coating formulas to increase water resistance [14].

Finishing

Modern finishing may include varnishing with a clear spirit varnish to improve durability, to protect a final printed surface, and to increase luster. However, the amount of varnish gloss depends on the hold-out quality of the coating, which is enhanced by a binder having good film-forming properties (such as casein as opposed to starch) and a less absorbent pigment (such as fine clay rather than calcium carbonate).

Modern coated papers, formerly flint and friction calendered (which used talc as a finishing pigment), are today usually supercalendered (sometimes with emulsions including wax, soap, or polyethylene), which subjects the coating to pressure-polishing, improving smoothness and gloss, with the least reduction in bulk and light-scattering coefficient [14]. The level of gloss is influenced

primarily by three factors. One factor affecting gloss is the supercalendering process, which imparts different effects depending on the type of calender used (e.g. having stacks of 10–12 soft cotton-filled rollers); the number of nips through which the sheet is passed; the pressure, which may range from 400 to 2000 pounds per linear inch; the speed, which may reach 800 meters per minute or more; and the temperature, since heat increases supercalendering action by softening the web and plasticizing the binder. A second factor affecting gloss is the binder and its amount (higher ratios lower gloss), as well as type (i.e. starch produces a dull gloss while resins and latexes are glossiest, although latexes have a tendency to “blacken” from too close compression and the resultant loss of light-refracting pigment surfaces). A third factor affecting gloss is the pigment and its moisture content, which along with heat serves to soften and plasticize the coating so that supercalendering does not crush the paper structure below (although high moisture can also cause “blackening”); pigment particle shapes, such as clay’s plate-like particles; and pigment particle size (the finer, the higher the gloss in general) [13,14].

Calendering lowers the strength of coated papers one wax level in the TAPPI Standard Dennison Wax Pick Surface Strength Test, and can cause unwanted patterns of ridges and valleys if coatings become over-plasticized, as with some high speed roller-coating systems. Another polishing technique is cast-coating, which can be done on or off the papermaking machine. It requires pressing a freshly coated paper against a highly polished nickel or chromium plated drier; after the paper dries, it is stripped off (wax is sometimes added to aid in stripping). The technique, low-speed and high-cost, can be used with greater amounts of binder but yields a soft porous surface, susceptible to marring [14].

Conclusion

Variables of furnish (composition, size, refractive index, brightness, and pH of pigments particles, as well as type or amount of binders and additives), and of formation (application and calendering procedures), affect the physical structure of a pigment coating, which in turn affects the optical properties of a pigment-coated paper [13, 14]. Unfortunately, the structural and optical properties of a coating may also change as a result of degradation and subsequent conservation treatment, affecting the ultimate appearance of the coating. However, there are trends in the type of furnish materials and formation procedures employed in the production of coated papers that may aid in the characterization of pigment-coated papers requiring conservation treatment. By using the information on pigment elemental composition, size, refractive index, brightness and pH in Table I, coupled with binder analysis, conservators may be able to identify the type of pigment coatings with which they are confronted. By incorporating information on use, rawstock, brightness, and gloss set by the US Grading Standards, in Table II, they may be able to identify the grade of a given pigment-coated paper. In understanding the effects of furnish and formation procedures on coating properties, and by correlating the information in Tables I and II, conservators may be able to better anticipate and evaluate changes in properties that might occur from conservation treatments.

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Abstract

Using information derived from a study characterizing types of pigment-coated papers, the authors investigated the effects of various treatments on selected examples. To evaluate the effects of some solvent application techniques on pigment-coated papers, two projects were designed. The first project was a preliminary investigation, testing papers hand-coated with traditional recipes, to subjectively compare the effects of different stain removal solvents (water, ethanol, acetone, and toluene) and application techniques (poultice, immersion, and suction disk). Findings, based on SEM imaging, indicate that some application techniques and some solvents can cause microfissures or loss in coating material. The second project was a statistical study using contemporary machine-coated papers to provide reproducible data on the effect of two treatments which have been used for cleaning dirt, stains, or accretions from pigment-coated papers, namely aqueous immersion and blotter-poulticing, followed by air- or blotter-drying. Findings evaluated changes detected by SEM imaging and measured by color (CIE L*a*b*) and gloss (85° angle). SEM imaging revealed more surface disruption in blotter-poulticed and blotter-dried samples. Immersed and air-dried samples underwent a greater unit reduction in gloss than poulticed, blotter-dried samples. The glossiest paper underwent the greatest unit reduction in gloss following all treatments.

Keywords

Coated papers, prepared grounds, chromolithographs, solvent applications, poultice, aqueous immersion, drying, stain removal, accretion removal, color, gloss, technology, history, treatment trials, research design

Pigment-Coated Papers II: The Effects of Some Solvent Application Techniques on Selected Examples

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Introduction

Pigment-coated papers can pose particular problems for collections and conservators because of their special formulations. Such formulations, which were the focus of an earlier study, render pigment coatings especially susceptible to damage from abrasion, flaking, fingerprint and oil stains, water stains and blocking, and adhesive and tape accretions and staining [1-5]. Ironically, their special formulations also render the pigment coatings susceptible to damage from some of the conservation treatments which might be used to correct the problems noted above. This second study was developed to evaluate some of the effects of various application techniques of solvents on selected examples of pigment-coated papers. It consists of two projects described below, following a brief overview of treatment research and design.

Treatment Research and Design

Treatments for pigment-coated papers, published in the conservation literature, have included the use of organic and aqueous solutions applied by steam, brushes, and poulticing for the removal of stains and accretions [3,4,5,7,8]. Similar treatments used by the authors have been found to be very successful, although microscopic examination has indicated that organic and aqueous solutions may cause the break up, microfissuring, or loss of pigment coatings (see Figs. 1 and 2)[1,8]. Consequently, two treatment projects were developed, as indicated in the research design.

Research design for pigment-coated paper projects.

A. Characterize and select pigment-coated paper samples for treatment testing (hand-coated and machine-made pigment-coated papers).

B. Select treatment procedures to be tested.

Project 1: Effects of stain removal solvents & application techniques on hand-coated papers.

Water	Ethanol	Acetone	Toluene	Untreated control
Application techniques:				
Immersion	Poultice	Suction disk		

(Note: For each paper type each sample was tested once.)

Project 2: Effects of accretion removal techniques on machine-coated papers.

Immersion		Poultice		Untreated control		
A1	A3	A3	B1	B2	B3	C1 C2 C3
Air Blot	Air Blot	Air Blot	Air Blot	Air Blot	Air Blot	

(Note: For each paper type each sample under categories A1-C3 was tested 3 times.)

C. Evaluate general findings based on changes in appearance (SEM imaging) and/or properties (color/brightness and gloss).

The first project was a preliminary study using SEM imaging to compare the effects of solvents (water, ethanol, acetone, and toluene) and application tech-

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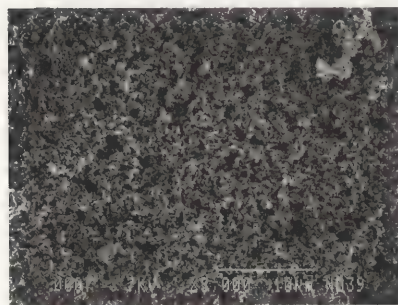


Fig. 1a: Hand-coated paper with calcium carbonate:Liquitex rabbit skin glue (1:3) applied in 5 coats

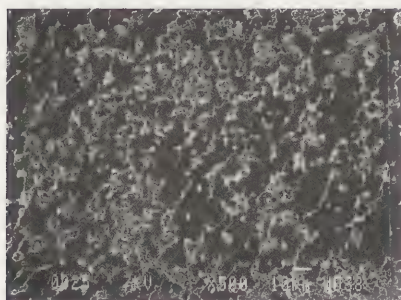


Fig. 1b: After hand-burnishing

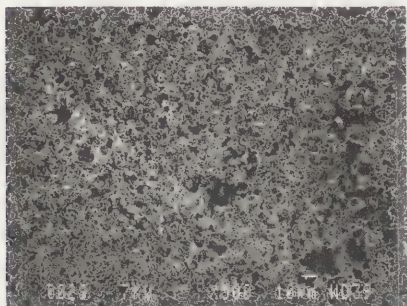


Fig. 1c: After application acetone by suction table to lower left corner; shows break-up of burnished surface

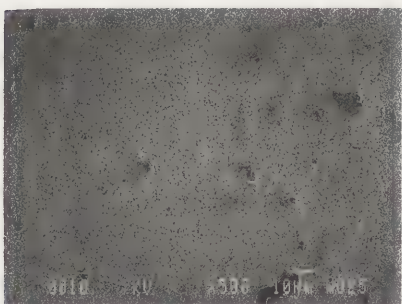


Fig. 2a: Hand-coated paper with zinc oxide:Liquitex rabbit skin glue (2:3) applied in 5 coats

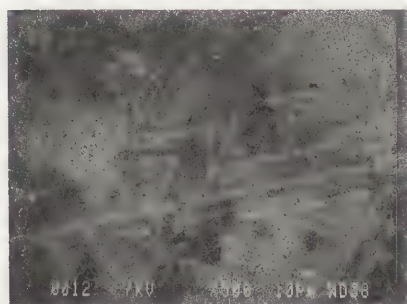


Fig. 2b: After hand-burnishing

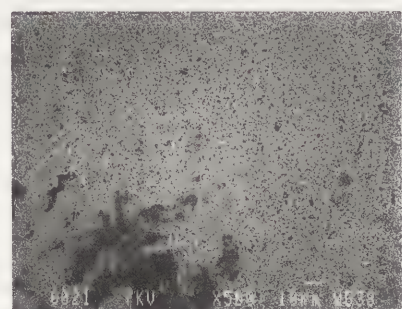


Fig. 2c: After application acetone by immersion to lower left corner; shows break-up of burnished surface

niques (poultice, immersion, and suction disk), used in conservation for stain removal, on traditionally hand-coated papers. The second project was a statistically controlled study comparing the effects of accretion removal techniques (aqueous immersion and blotter-poulticing) on contemporary pigment-coated (machine-coated) papers. Changes in appearance of the pigment coating with respect to surface structure were observed by SEM imaging; brightness was measured by colorimetry; and gloss was measured by a glossmeter. The following summaries for each of the two projects describes the A) paper samples characterized, B) treatment procedures used, and C) general findings.

Project 1: Effects of stain removal solvents and application techniques on hand-coated papers

A) Paper Samples Characterization: A survey of traditional recipes provided the basic information for sample preparation [9]. The sample papers were hand-coated with combinations of calcium carbonate, zinc oxide and barium sulfate in binders of gum, glue, and acrylic. A machine-coated paper composed of barium sulfate and calcium carbonate in an acrylic binder was examined and tested as a comparison exemplifying a contemporary pigment-coated paper. Six test papers were prepared by hand-brushing a paper support (machine-made wove paper of high alpha cellulose rawstock) with one of each of the following formulas, made with reagent grade compounds:

1. calcium carbonate:Liquitex rabbit skin glue (1:3) applied in 5 coats
2. calcium carbonate:gum arabic (1:2)
3. zinc oxide:Liquitex rabbit skin glue (2:3) applied in 5 coats
4. zinc oxide:gum arabic (2:3)
5. zinc oxide:Liquitex gel acrylic medium
6. barium sulfate and calcium carbonate : Liquitex gel acrylic medium

B) Treatment Procedures: Four solvents (water, ethanol, acetone, and toluene) were applied by three techniques (immersion, poultice, and suction disk) to each sample of paper using the techniques described below:

Immersion technique: For the immersion technique, the end of each sample was dipped into a 3 mL deep solution of solvent and held there for 3 seconds. The sample was then removed and allowed to air-dry.

Poultice technique: The poultice technique consisted of placing diatomaceous earth saturated by solvent (approximately 1-2 mL solvent to 0.3 grams diatomaceous earth, depending on solvent) on the front of each paper sample lying on a non-absorbent support.¹ The poultice covered an area approximately 5mm in diameter, and contrary to normal practice, the wet poultice was not surrounded by dry poultice to diffuse the transition from wet to dry areas. The poultice was allowed to air-dry before being removed by an air bulb and brushing.

Suction Disk technique: The suction disk technique consisted of applying three drops of each solvent locally by dropper on a 15 cm fritted glass bead disk (masked off with polyester film), which can reach a pressure of c. 25" Hg.

C) General Findings: SEM imaging (described below) indicated that certain application techniques caused changes to some papers. For instance, acetone applied by suction table cause the break-up and/or loss of the burnished surface of a paper hand-coated with calcium carbonate and Liquitex rabbit skin glue (Fig. 1). A similar change occurred when acetone was applied by immersion to a paper hand-coated with zinc oxide and Liquitex gel acrylic medium (Fig. 2). The aqueous poultice applications used in this study also caused microfissuring of some pigment-coated surfaces, especially the machine-coated sample [1,4,9].

Project 2: Effects of selected accretion removal techniques on contemporary machine-made pigment-coated papers

A) Paper Sample Characterizations: Several contemporary machine-made pigment-coated papers were selected and assigned codes such as those in quotes below. The papers were supplied by various (anonymous) manufacturers, whose accompanying literature described the papers as follows:

- "B": Machine-made in France as "Special Point d'Argent: Calligraphie" (recommended by manufacturer for silver point drawings).
- "C": Machine-made 100% rag paper with neutral pH. Smooth, clay-coated; recommended for silverpoint drawing.
- "F": Machine-made glossy, light weight stock, available in 28 colors.
- "K": Glossy white text-weight paper recommended for illustrations and ink drawings.
- "L": Machine-made in Germany; smooth, glossy surface on 2 ply, 10 point card stock.
- "Q": Machine-made with fine clay coating. Ivory color, recommended for silverpoint drawing.
- "R": Machine-made 100% rag paper with neutral pH. Smooth, clay-coated (2 sided); glossy on one side and matte on the other. Recommended for offset printing but not silverpoint drawing.
- "S": Machine-made paper with smooth clay coating recommended for silverpoint drawing.

The machine-coated papers were also characterized in-house by analysis of pigments and binders using the following instrumentation techniques and measurements:

SEM: SEM imaging of coating surface and cross-section morphology, and SEM/EDS analysis of pigments, were carried out on a Jeol JXA - 840 A scanning electron microscope with Tracore Northern TN 5502 energy dispersive x-ray analysis system. The samples were mounted on aluminum stubs and gold coated for imaging, and on carbon stubs and carbon coated for elemental analysis.

FTIR: FTIR analysis of binders was carried out on a Mattson Cygnus 100 Fourier Transform Infrared Spectrophotometer with a Spectratech IR-Plan Microscope. Surfaces of coated papers were analyzed by reflectance, or alternately micro samples of coatings were removed and pressed into thin films in a diamond anvil cell for analysis by transmission.

Colorimetry/Brightness: Color (specular reflectance included) of coatings was measured with the HunterLab Ultrascan Spectrocolorimeter (D_{65} , 10° observer, diameter of area of view 1.2 in) using the CIE $L^*a^*b^*$ color notation, where L^* represents the degree of brightness (100 white, 0 black), a^* the degree of redness (positive numbers) or the degree of greenness (negative numbers) and b^* the degree of yellowness (positive numbers) or the degree of blueness (negative numbers). Three measurements were taken per sample and averaged. Brightness was calculated for the untreated papers by the following equation: $B = 0.01L^2 - bL/70$. Ultrascan measurements are comparable to GE Brightness used by industry (see Tables in previous article), which measure reflectance at 457nm using a tungsten source, except that Ultrascan measurements will be higher when optical brighteners are involved.

Gloss: Gloss of coatings was measured with a Dr. Lange Labor-Reflektometer RL at angles of 20° , 60° and 85° . Three measurements for each angle were taken per sample and averaged.

The elemental compositions of the contemporary machine-coated papers are listed in Table I. This was compared with the previous article's Table I of the elemental composition of common coating pigments. The earlier table indicates the refractive index and general size of pigment particles as used in the paper coating industry, which along with particle shape contribute to the brightness, gloss, and opacity of the final coat. For instance, refractive index (n) influences a pigment's ability to refract light, contributing to opacity, which is important for reducing print show-through in contemporary papers. Size (microns or μm) also affects a pigment's ability to refract and reflect light; as the particle size decreases, opacity increases [10]. Particle size also affects surface smoothness and contributes to gloss, depending on porosity, compactness, etc. A size of 0.12 may be best for ink holdout, while 0.2 might be best for gloss, but 0.5 may have the best combination of gloss and light scatter [11].

Table I. Elemental composition of selected machine-coated papers based on SEM/EDS.

Papers	Al	Si	K	Ti	Ca	S	Ba
"B"	—	+	—	—	+	+	+
"C"	+	+	—	+	—	—	—
"F"	+	+	—	+	+	—	—
"K"	+	+	+	—	+	+	—
"L"	+	+	+	—	+	+	—
"Q"	+	+	—	+	+	—	—
"R"	+	+	—	+	+	—	—
"S"	+	+	—	+	+	—	—

Based on the comparison of elemental compositions shown in both Tables I (of this and the previous article), the contemporary machine-coated papers can be divided into three groups. The first group ("B") is made primarily of barium sulfate (Ba, S), perhaps with talc (Si, Ca) or gypsum (Ca, S). The second group ("K" and "L") contain primarily clay (Al, Si, K) and gypsum (Ca, S). The third group (the remainder) contain primarily clay (Al, Si) and talc (Ti, Ca) or titanium dioxide and calcium carbonate. The pigment-coating compositions of these papers were compared with the composition of several pigment-coated chromolithographs undergoing contemporaneous conservation treatment [6]. Based on these comparisons, one paper from each of the three groups was chosen for treatment trials and testing. The three selected contemporary machine-coated papers, designated by the codes "B," "S," and "L," are described in Table II. By comparing the information in Table II of this article with the information

Table II. Characterization of selected machine-coated experimental papers, with Ultrascan brightness (converted from L* spectral reflectance value) and Reflektometer gloss (at an 85° angle).

Papers	Rawstock (estimated percentages)	Pigment composition		Binder (FTIR)	Bright- ness (Hun- ter)	Appearance	85° gloss
		SEM/EDS	FTIR				
"B"	100% ground hardwood and softwood (estimate)	Ba, S, Ca	sulfate, some clay	protein, resin	91.66	matte, smooth	18.5
"S"	40% chemical, 50% mechanical wood pulp, 10% rag (est.)	Ti, Si, Al, Ca	clay, calcium carbonate	styrene acrylic resin	85.08	matte, slightly rough	11.8
"L"	85% chemical softwood, with some chemical hardwood, 15% rag (est.)	Si, Al, Ca, S, K	clay	protein, acrylic	89.65	very glossy, smooth	96.9

in Table II of the previous article, the respective grades of the papers may be estimated. For instance, the make-up of paper "B" suggests it may be a lower grade paper (Grade 4 or 5); "S" may be a middle grade (Grade 2 or 3); and "L" may be a higher grade (Grade 1).

B) Treatment Procedures: The treatment procedures compared effects of water applied by two techniques that might be used to remove accretions or to humidify a piece prior to flattening. The two treatment techniques were immersion and poulticing with a damp blotter. These two treatments were selected to represent

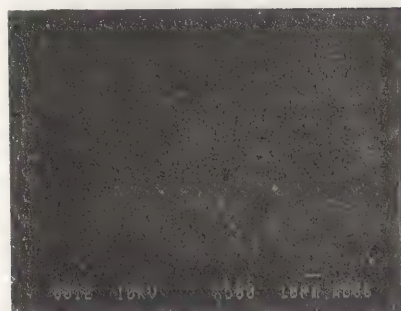


Fig. 3a: Machine-coated paper "B" before treated

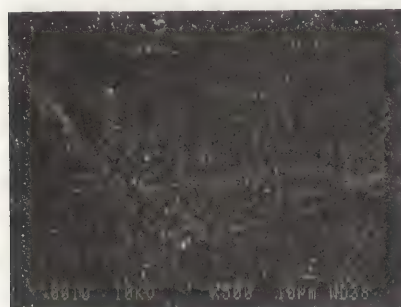


Fig. 3b: After immersion and air-drying

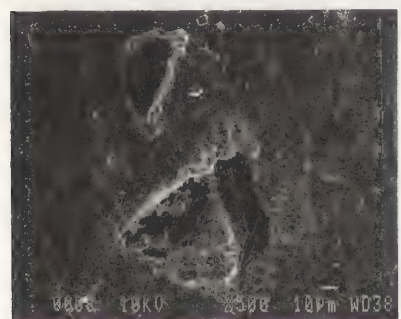


Fig. 3c: After blotter-poulticing and blotter-drying

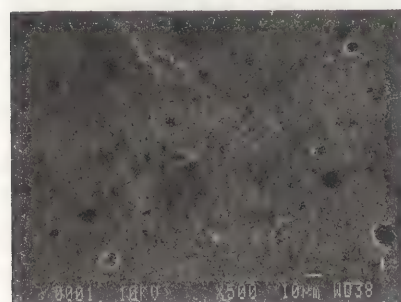


Fig. 4a: Machine-coated paper "S" before treated

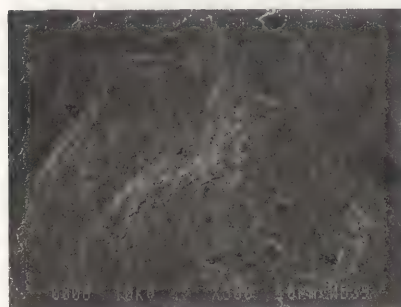


Fig. 4b: After immersion and air-drying

differences in amount of solvent absorption, exposure time to solvent, and direction of application and evaporation. For example, aqueous immersion may result in greater penetration, longer exposure, and more lateral movements of compounds as compared to aqueous poulticing. Half of the samples were exposed to a five minute immersion treatment in deionized water, while the other half of the samples were poulticed with a damp blotter for five minutes. Half of each set of the treated samples were air-dried and the other half were dried in a blotter press. The experimental conditions are outlined in Appendix A, with details of the procedures as follows:

Immersion Procedure: The samples were immersed in deionized water on a polyester web (nonwoven, with a smooth surface, 5 mil) on a polypropylene screen. The samples remained immersed for five minutes. The screen with web and samples was lifted out of the water and allowed to drain for two minutes. Half of the samples were lifted on the polyester web to a unbuffered blotter on a felt and were allowed to air-dry totally. Appearance measurements (color and gloss) were taken after two days. The other half of the samples were placed onto an unbuffered blotter on a felt and allowed to air-dry for 5–10 minutes until all standing water on the surfaces of the papers evaporated. The unbuffered blotter under the samples was replaced by a dry unbuffered blotter and these samples were then covered with polyester web, unbuffered blotter, and felt, and were blotted with hand pressure. Both top and bottom unbuffered blotters were changed and the ensemble was placed for five minutes in a "press" under a felt and ½ inch thick piece of plexiglass (less than 1 PSI). The unbuffered blotters were changed again after one hour and returned to the "press". The polyweb and unbuffered blotter were changed the next day and returned to the "press." Appearance measurements (color and gloss) were taken after two days.

Poultice Procedure: The unbuffered blotter used for poulticing was dampened by immersing it on a screen in a tub of deionized water. The screen was removed and the unbuffered blotter was drained on the screen for two minutes. A piece of 4 mil polyester film was placed on the unbuffered blotter resting on the screen and then the unbuffered blotter was flipped over so that the polyester film was on the bottom. The unbuffered blotter was allowed to sit for five minutes to enable standing water to evaporate for more even moisture distribution. The unbuffered blotter was then flipped over onto the samples which were against a formica countertop and the polyester film was removed. A felt and a ½ inch thick piece of plexiglass were place on the unbuffered blotter-poultice for 5 minutes. After the plexiglass, felt, and damp unbuffered blotter were removed, the wet samples were exposed to the air for two to five minutes, until all standing water on the surfaces of the papers evaporated. Half of the samples were left to air-dry totally. Appearance measurements were taken after two days. The other half were moved to a blotter "press" made up, from the bottom up, of the formica counter, felt, unbuffered blotter, polyester web, sample, polyester web, unbuffered blotter, felt, plexiglass (less than 1 PSI). The samples were left overnight in the press. The next day the polyester web and unbuffered blotter were changed and the ensemble was returned to the "press." Appearance measurements were taken after two days.

C) General Findings: Changes in the papers after treatment were assessed by SEM imaging and by measuring optical properties of color and gloss, as follows:

SEM: All papers were found to have undergone surface changes following all treatments when viewed with a scanning electron microscope. As compared to the untreated controls, immersed air-dried samples generally showed less change than the poulticed blotter-dried samples (Figs. 3–5). For the barium containing paper "B," the immersed samples generally exhibited raised areas and microfissures. In comparison to the untreated control (Fig. 3a), the immersed air-dried samples showed fibers more exposed (Fig. 3b), while the immersed blotter-dried samples showed disturbed areas and apparent lifting of the surface. The poultice air-dried samples showed a disturbed surface characteristic of lifting and delamination, while the poultice blotter-dried sample showed microfissuring, lifting of coating, and wrinkles (Fig. 3c). For paper "S," the immersed samples were found to have a more pitted surface with more exposed fibers as compared to

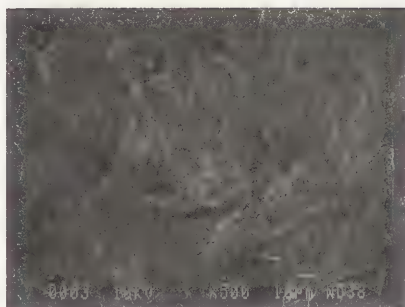


Fig. 4c: After blotter-poulticing and blotter-drying



Fig. 5a: Machine-coated paper "L" before treated

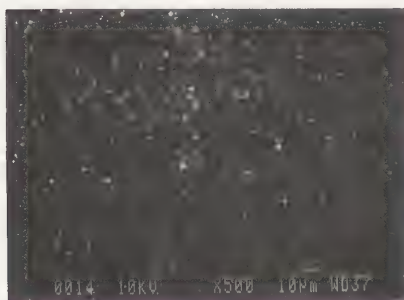


Fig. 5b: After immersion and air-drying

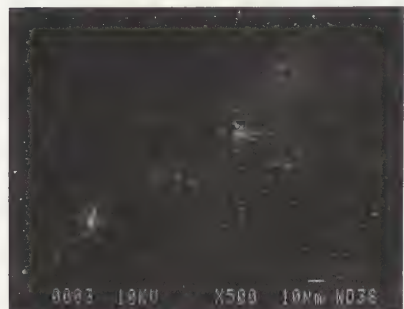


Fig. 5c: After blotter-poulticing and blotter-drying

the untreated control (Fig. 4a). The immersed air-dried samples also exhibited microfissuring (Fig. 4b), while the poulticed blotter-dried samples had microfissures and depressions (Fig. 4c). For glossy paper "L" small holes or microfissures were found in all treated samples (Figs. 5a-c).

Colorimetry: All of the papers exhibited darkening (decrease of L^* or brightness) and yellowing (increase in b^* , Fig. 6). However, the changes are all less than one unit and could not be considered visually significant, regardless of statistical significance. Greater darkening (and yellowing) occurred with the immersed air-dried samples, followed generally by the immersed blotter-dried samples.

Gloss: All samples showed a significant reduction in all gloss measurements regardless of whether the measurement was made at an angle of 20, 60, or 85 degrees. Gloss reduction tended to be greatest following immersion and following air-drying (Fig. 7). The greatest change was measured at 85 degrees and for

Fig. 6: CHANGES IN COLOR (b^*)

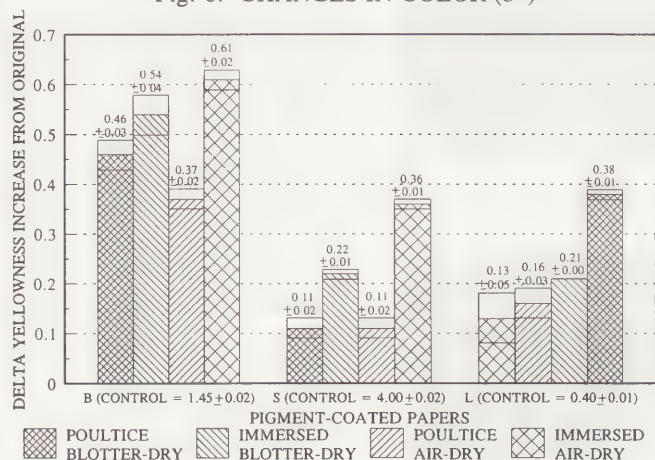


Fig. 6: Colorimetry

Fig. 7: CHANGES IN GLOSS (85°)

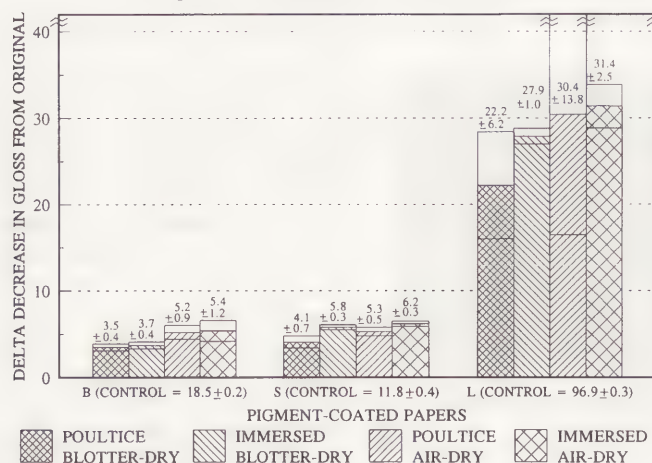


Fig. 7: Gloss

the glossiest paper ("L"); standard deviations were large for this paper, especially for the poulticed measurements. This suggests that the gloss changes to this paper were not uniform. (See Appendix B for gloss measurements).

Conclusion

With respect to solvent application techniques, SEM imaging indicated that specific application techniques could cause changes in the surfaces of some papers. For instance, acetone applied by suction table caused the break-up, microfissuring, and/or loss of the burnished surface of a paper hand-coated with calcium carbonate and Liquitex rabbit skin glue (Fig. 1). A similar change occurred when

acetone was applied by immersion to a paper hand-coated with zinc oxide and Liquitex gel acrylic medium (Fig. 2). The aqueous poultice applications used in this study also caused microfissuring of some pigment-coated surfaces, especially the machine-coated sample [1,4,8].

Aqueous immersion and blotter-poulticing, followed either by air-drying or blotter-drying, of three different types of contemporary machine-made, pigment-coated papers, caused changes in surface appearance and significant reductions in gloss and color/brightness (increased darkening and yellowing). The greatest structural changes, as observed by SEM imaging, occurred in the blotter-poultice samples, especially for less glossy papers. The greatest unit reduction in gloss, as measured instrumentally, occurred in the glossiest paper and was most irregular for the poulticed samples. Findings suggest that while aqueous blotter-poulticing and blotter-drying may be appropriate for some pigment-coated papers, other procedures might cause less surface change to highly glossy coated papers.

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Note

1. Diatomaceous earth (hydrated silica from diatom plant skeletons) was selected as a poultice for its working properties since, unlike gel poultices (methylcellulose, agarose, starch paste, or hydroxypropylethylcellulose) it can be mixed with aqueous or non-aqueous solvents to form a plaster or paste that absorbs solutes as it dries to a powder, which can then be brushed off. It is more cohesive than fused silica. It is whiter than Fuller's earth, which is formed from hydrated silicates of magnesium, calcium, aluminum, or other metals. It is more controllable than organic solid poultices such as powdered cellulose, paper, or cotton.

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Appendices

Appendix A. Experimental conditions and labelling. Each treatment trial was conducted three times and each resultant sample was measured three times for statistical accuracy.

Contemporary pigment coating	S	L	B
Control (C)	1 = C	14 = C	27 = C
Immerse/airdry (IAD)	2 = IAD.1 (3 meas)	15 = IAD.1 (3 meas)	28 = IAD.1 (3 meas)
	3 = IAD.2 (3 meas)	16 = IAD.2 (3 meas)	29 = IAD.2 (3 meas)
	4 = IAD.3 (3 meas)	17 = IAD.3 (3 meas)	30 = IAD.3 (3 meas)
Immerse/blotter (IBD)	5 = IBD.1 (3 meas)	18 = IBD.1 (3 meas)	31 = IBD.1 (3 meas)
	6 = IBD.2 (3 meas)	19 = IBD.2 (3 meas)	32 = IBD.2 (3 meas)
	7 = IBD.3 (3 meas)	20 = IBD.3 (3 meas)	33 = IBD.3 (3 meas)
Poultice/airdry (PAD)	8 = PAD.1 (3 meas)	21 = PAD.1 (3 meas)	34 = PAD.1 (3 meas)
	9 = PAD.2 (3 meas)	22 = PAD.2 (3 meas)	35 = PAD.2 (3 meas)
	10 = PAD.3 (3 meas)	23 = PAD.3 (3 meas)	36 = PAD.3 (3 meas)
Poultice/blotter (PBD)	11 = PBD.1 (3 meas)	24 = PBD.1 (3 meas)	37 = PBD.1 (3 meas)
	12 = PBD.2 (3 meas)	25 = PBD.2 (3 meas)	38 = PBD.2 (3 meas)
	13 = PBD.3 (3 meas)	26 = PBD.3 (3 meas)	39 = PBD.3 (3 meas)

Appendix B. Data: Gloss, 85 degrees (standard deviations).

	S	L	B
Absolute			
Control (C)	1 = 11.8 ± 0.4	14 = 96.9 ± 0.3	27 = 18.5 ± 0.2
Delta			
Immerse/airdry (IAD)	2-4 = 6.2 ± 0.3	15-17 = 31.4 ± 2.5	28-30 = 5.4 ± 1.2
Immerse/blotter (IBD)	5-7 = 5.8 ± 0.3	18-20 = 27.9 ± 1.0	31-33 = 3.7 ± 0.4
Poultice/airdry (PAD)	8-10 = 5.3 ± 0.5	21-23 = 30.4 ± 13.8	34-36 = 5.2 ± 0.9
Poultice/blotter (PBD)	11-13 = 4.1 ± 0.7	24-26 = 22.2 ± 6.2	37-39 = 3.5 ± 0.4

Abstract

The color change of paper aged under various conditions of temperature and relative humidity is studied, and the effectiveness of washing for removing colored degradation products is assessed. Color production occurs in a manner typical for the deterioration of organic materials under conditions ranging from 50–90°C and from 30–80% relative humidity at three specific dew points. The rate of color change and the shape of the color change curves vary with the specific conditions. The best single predictor of color change is dew point.

Color change can be partially reversed by washing, but the degree of reversal decreases with more severe degradation. Those samples with the greatest color change had the lowest percentage of color removed by washing. In addition, the aging conditions affect the degree to which color change can be reversed by washing. Samples aged under different conditions, but with similar color change, have different proportions of soluble colored material.

An increased dew point resulted in increased color production. If the results found for the artificial aging conditions studied apply to room condition, and if the color change results are found to be characteristic of other chemical degradation processes, then dew point would be the best predictor of chemical stability in storage. To minimize deterioration, therefore, the storage environment should be based upon the lowest feasible dew point rather than on the choice of a specific relative humidity.

Keywords

Paper, cotton, cellulose, artificial aging, color, washing, water, dew point

Changes in Paper Color due to Artificial Aging and the Effects of Washing on Color Removal

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Introduction

Temperature and relative humidity (RH) play very important roles in the aging of paper. They influence both the *rate* at which paper ages and the *way* it ages. The degradation of paper involves a number of types of reactions, primarily hydrolysis and oxidation. The rate at which each reaction occurs can vary independently of the others. Thus, even if the same reactions occur under two different sets of aging conditions, the relative rates of the reactions may be very different. Some of these reactions cause changes in the color of the paper.

Earlier work demonstrated that dry and moist aging produce very different mixtures of soluble degradation products^{1,2}. The mixture of products produced during moist aging includes a large proportion of hydrolysis reaction products, while the result of dry aging is both a smaller proportion of hydrolysis products and a smaller total quantity of soluble products.

Knowledge of how environmental conditions influence the aging of paper is important for several reasons. The conservation treatment of aged paper objects is influenced by the condition of the paper and the known or deduced history of its aging. The choice of environmental conditions for storage should be based, in large part, on how the conditions will affect the aging of the paper. Accelerated aging conditions used to evaluate either materials or the effects of treatments should be chosen so that the accelerated aging conditions reproduce natural aging as closely as possible, speeding up the rate of aging without changing the nature of the aging process.

When examined for treatment, the evaluation of artifacts is based on their appearance and feel, of which color is a large part. This is especially so with paper. Color also is the main visual cue to the state of degradation or age of paper. Conservators use a subjective evaluation of color to determine the degree of deterioration and to help in deciding whether washing would be a useful treatment to increase the effective life of the artifact. In a study in which 18 historic papers were washed and evaluated, the subjective perception was that washing increased the "health" of most of the specimens (Vitale, 1992a). Health was correlated with averaged rankings of both the Yellowness Index _{E313} and work (area under stress-strain curve)^{3,4}.

In recent work, washing was found to alter "as-manufactured" mechanical properties and "dried-in" strains of paper^{5,6}. This suggested that while washing is a beneficial treatment it is not without its liabilities. This study, on the other hand, suggests washing is desirable in many cases that would normally be considered marginal because the color of the sheets had not changed dramatically enough to warrant washing.

Relative humidity, temperature, and dew point

In air with any concentration of water vapor, the temperature to which it must be cooled to cause water vapor to condense to liquid is the *dew point*. The dew point specifies the absolute water vapor concentration in the air. Relative humidity is the ratio of this absolute water vapor concentration to the maximum water vapor concentration possible at a specific temperature. The maximum possible water vapor concentration increases with temperature. Air with a specific absolute water vapor concentration (dew point) has a lower relative humidity at a higher temperature.

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Literature

Changes in the color of cellulose have been studied in the past^{7,8}. The development of color was associated primarily with the oxidative introduction of an aldehyde group in the anhydro-glucose ring at the #6 carbon or the oxidation to a ketone at either carbon #2 or #3. Arney and Chapdelaine demonstrated that there is a relationship between yellowing and acidity developed during aging, and the change in reflectance at 500 nm is linear both in the presence and absence of oxygen⁹. Spinner has reviewed the source of color reversion in common manufactured papers¹⁰. Gray has identified a relatively constant activation energy for changes in brightness (TAPPI A-452m-58) for a variety of modern manufactured papers¹¹. Hon has presented thorough reviews of possible sources of color and color reversion¹².

The existing work often is concerned with paper bleaching and color reversion, or the estimation of paper permanence, and uses color measurement units not directly traceable to human perception. These studies generally do not consider the aging of paper beyond the degree of change that would result in the loss of its commercial value. Conservators often deal with art objects or historic artifacts that exhibit a much greater degree of deterioration.

While comments on change in color (brightness, reflectance at a specific wavelength, ΔE CIE $L^*a^*b^*$, or Yellowness Index) are included in many conservation science articles on paper (among many) the relationship between the change in color ΔE (CIE $L^*a^*b^*$) and a range of temperatures and relative humidities is still unclear^{13,14}.

Experimental: aging conditions and duration

Ten samples each of two cotton papers were aged under seven different temperature and relative humidity conditions (See Table I). Samples of each paper were removed from each aging chamber after varying lengths of time; aging of remaining samples continues.

Table I. Conditions and times of aging for the Whatman #1 and CAL cotton paper samples.

Temperature °C	RH %	Dew point °C	Days of aging
90	50	74.0	2, 5, 8, 12, 20, 34, 49, 69, 105, 278
80	77	74.0	2, 5, 8, 12, 20, 34, 49, 69, 105, 278
80	32	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
70	50	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
60	80	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
60	30	36.9	56, 157, 323, 531, 811, 1203
50	50	36.9	56, 157, 323, 531, 811, 1203

The temperature in each chamber was maintained and monitored with a copper constantan thermocouple (type T) connected to a proportional controller. The relative humidity was maintained by a constant flow of filtered air conditioned to a selected dew point (absolute water vapor concentration) by bubbling it through a water bath maintained at the appropriate temperature. The humidified air from each saturator flowed through parallel heated supply lines to a group of two or three chambers, each maintained at a different temperature higher than the dew point. The relative humidity in each set of chambers was adjusted initially by monitoring the dew point of the humidified air supply with a General Eastern dew point hygrometer, system 1100D with a 1111D sensor. Once set, the relative humidity in each chamber subsequently was monitored with electronic RH sensors, model PC-2101, manufactured by Thunder Scientific Corp., Albuquerque, NM. Temperatures in the sample chambers and water bath were monitored using standard type T thermocouples and digital thermometers.

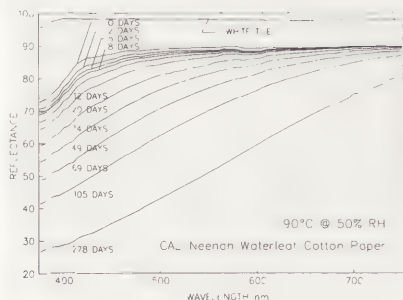


Figure 1. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days with the HunterLab white tile reference standard.

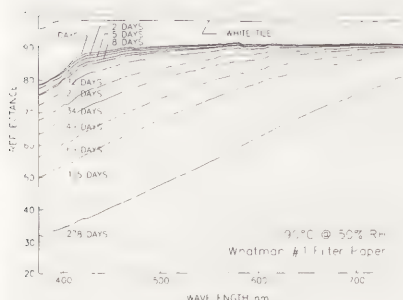


Figure 2. Reflectance spectra, 375–750 nm, of the Whatman #1 filter paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days with the HunterLab white tile reference standard.

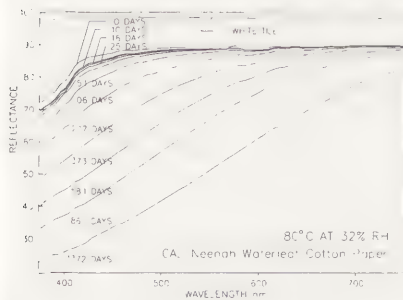


Figure 3. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 80°C @ 32% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

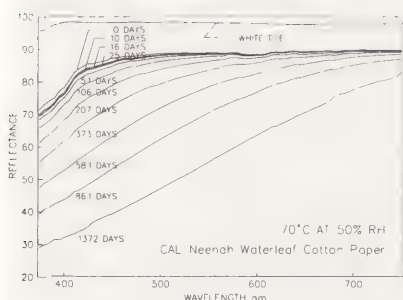


Figure 4. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 70°C @ 50% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

Washing

Approximately 2.5 in² portions of selected samples were washed in ultrapure deionized water for one hour, drained for 1–2 minutes and dried between blotters at a pressure of 690 Pa (0.10 psi). The deionized water was processed through Hydroservices Corporation mixed-bed and activated charcoal columns. In-pipe water quality was 18.1 megaohms at 20°C. No pH measurement was made, due to the inaccuracy of such a measurement caused by the absorption of atmospheric carbon dioxide and reference electrode solution.

Ultrapure water, in relation to other common water types, has been shown to have little or no effect on the mechanical and chemical properties of historic and modern paper^{15,16}. This suggests that the effect of washing with ultrapure water should not be different than other types of water for removing soluble components, and that it has no specific effects which would alter the chemistry or interfiber bonds of the paper uniquely.

Color Measurements

The reflected spectrum (375–750 nm) of each sample was measured using a Hunter Lab Ultrascan spectrometer with a D65 light source, 10° viewing angle, 0.375 in² sphere opening, in the RSIN mode (reflected specular light included). The entire spectral curve was recorded, and CIE 1976 L*a*b* values and the ASTM Yellowness Index E_{313} were calculated. Measurements taken from five different spots on each sample were averaged and the standard deviations calculated. The differences in total color, ΔE , as well as ΔL^* , Δa^* and Δb^* were calculated for each aged sample relative to the control sample¹⁷. The ΔE for the aged and washed samples was calculated relative to the washed control. The ΔE determination for the difference between washed minus aged was calculated relative to the aged version of the washed sample.

Spectral reflectance from 375–750 nm was calculated as an average of the same five spectral readings for each aged, and aged and washed specimen. Selected examples of the spectral reflectance have been plotted in the same figure along with the HunterLab Instrument Standard D8 #7566 (2/88, Reston, VA) white tile standard. Small humps, peaks and other features are evident in these samples that do not appear in the spectra of the white tile.

The CIE 1976 L*a*b* scale is a human perception based, color axis system for defining a specific color by its location on three axes: a vertical axis and two intersecting perpendicular axes. L* measures lightness/darkness along the vertical axis, with 0 being black and 100 being white. The a* axis measures redness-greenness, with positive values indicating redness, and negative values indicating greenness. Similarly, b* values measure blueness-yellowness, with positive b* values indicating yellowness and negative b* values indicating blueness.

Materials

Two types of paper were used: (1) a waterleaf cotton paper prepared by Neenah Paper Company (Appleton, WI) for the Conservation Analytical Laboratory (CAL) and (2) Whatman #1 filter paper. The research paper from Neenah is a staple cotton fiber unsized sheet which is 0.004" thick. Fiber analysis (conducted by the Institute of Paper Science and Technology, IPST, formerly Institute of Paper Chemistry, IPC) determined that the paper is 91% cotton seed hair pulped from cotton knit cuttings in sodium hydroxide liquor, with 2.2% softwood and 6.7% hardwood, both pulped using predominantly the Kraft process.

The Whatman #1 filter paper is made from high alpha cellulose cotton linter pulp beaten and formed to 0.0069" thickness for an 11 micron particle capture size. No acid or alkaline wash or wet strength additives are used. Ash content is listed as 0.06%; cation content is 185 ppm Ca, 160 ppm Na, 7 ppm Mg, 5 ppm Fe; and anion content is 130 ppm Cl and 15 ppm S.

Results of aged (only) specimen data

Figures 1 and 2 plot the change in reflectance spectra for the CAL cotton and Whatman #1 specimens aged at 90°C@50%RH. The changes in the spectra

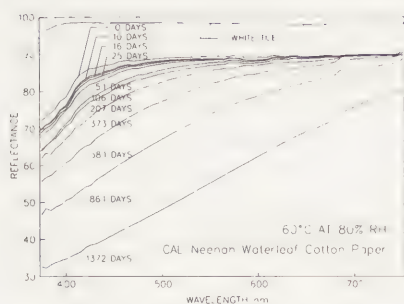


Figure 5. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 60°C @ 80% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

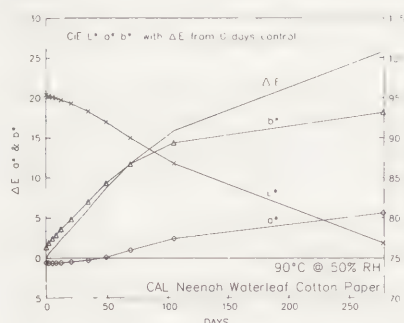


Figure 6. The CIE 1976 L^* , a^* , b^* and ΔE (from 0 days, control) data for the CAL cotton paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days. Note the second y axis for L^* on right.

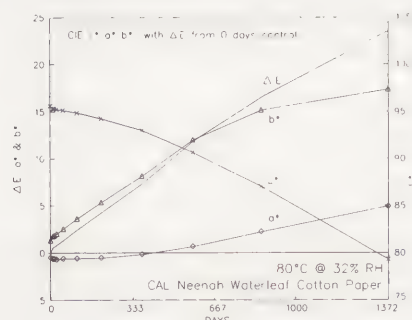


Figure 7. The CIE 1976 L^* , a^* , b^* and ΔE (from 0 days, control) data for the CAL cotton paper aged at 80°C @ 32% RH (dew point 55.5°C) for 0–1372 days. Note the second y axis for L^* on right.

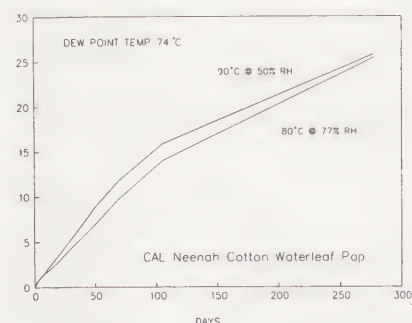


Figure 8. ΔE for the CAL cotton paper at dew point 74.0°C, 90°C @ 50% RH and 80°C @ 77% RH, aged for 0–278 days; note the near-parallel behavior.

that occur upon aging are typical of those obtained for all conditions (see Figures 3–5). The shoulder on the curve of the unaged papers (0 days) between 395–450 nm disappears as the aging process proceeds. Note that this feature does not appear in the spectral curve for the HunterLab WHITE TILE that is included in all figures. There are also features between 555–620 nm that also disappear during the aging process. In the spectra for samples aged longest in Figures 1 and 2 (278 days), new features appear around 380 nm, 420 nm and in the range 670–750 nm. While these features cannot now be attributed to a specific process or degradation product, it can be stated that two papers of different composition (cotton linters vs. cotton staple fibers) show the same loss and introduction of features. Note that the red (shorter wavelength) end of the spectrum changes less than the blue (longer wavelength) end. The increased absorption in the blue end of the spectrum causes the paper to appear yellower and darker. This is most clearly seen when ΔE , L^* , a^* , and b^* are plotted together, as in Figures 6 and 7.

Figures 3, 4, and 5 plot the reflectance spectra curves for the CAL cotton paper at 80°C@32%RH, 70°C@50%RH and 60°C@80%RH (55.5°C dew point) for the 0–1372 day aging series. The resemblance is remarkable, both within the 55.5°C dew point group and between the Whatman #1, 90°C@50%RH, samples in the 74.0°C dew point series (see Figure 2) and the 55.5°C dew point group.

When $L^*a^*b^*$ and ΔE values are plotted together in Figures 6 and 7 (CAL cotton 90°C@50%RH and 80°C@32%RH) the b^* (yellowness-blueness) value appears to control the trend of the ΔE plot. Note, also, that under these conditions at approximately 49 and 373 days of aging, respectively, the a^* value becomes positive and has a significant influence on the ΔE curve.

Figure 8 plots ΔE for the 74.0°C dew point group (90°C@50%RH and 80°C@77%RH) of the CAL cotton paper from 0–278 days of aging. The plots are remarkably similar both in shape and slope, increasing linearly at first and then tailing off.

Figure 9 plots ΔE for the 55.5°C dew point group (80°C@32%RH, 70°C@50%RH and 60°C@80%RH) of the CAL cotton paper for the 0–1372 day aging period. Although they deviate slightly during the initial stages of aging, the three curves become nearly parallel for the rest of the aging period. Note that curves for 70° and 80° exhibit the S-shaped curve (induction time, autocatalytic, steady state, and autoretardation) discussed by Feller¹⁸.

Figure 10 plots ΔE for the 36.9°C dew point group (60°C@30%RH and 50°C@50%RH) for the 0–1203 day period. Though very little change in color (note the ΔE scale) has occurred after 1203 days of aging (1.5 ΔE), there is some indication that these two plots also will reach parallel paths after a small initial deviation.

Figures 11 and 12 show the combined ΔE data for all aged series in the CAL cotton and Whatman #1 groups. Note that the results for both papers are almost identical. The Whatman #1 samples show a slightly more pronounced and longer induction period. The slightly darker values that the CAL cotton samples aged the longest have attained may be the result of a shorter induction period.

Aged & washed specimen data

Figures 13, 14 and 15 plot the data and Table II lists the changes in ΔE after washing for the three dew point groups of the CAL cotton paper. It can be seen in the data for the high dew point group that only a small portion (1.9–2.4 units) of the color change is reversed by washing after 69 days of aging and an even smaller reversal, 0.9–1.8 units, is realized after 278 days of aging (See fig. 13). Note that the aged, and washed & aged samples symbols (with dotted line tracing the difference) in the figures are superimposed over the aged curves for the purpose of providing a reference.

It can be seen in Figure 14 that washing the samples in the 55.5°C dew point group results in relatively constant absolute changes in ΔE . On average, there is a larger change in the 55.5°C group than for the 74.0°C dew point group

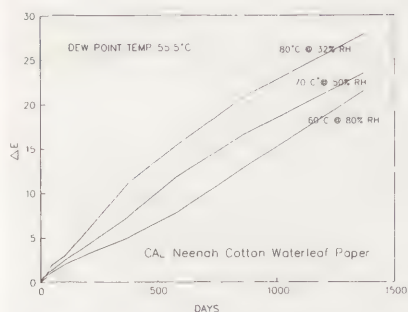


Figure 9. ΔE for the CAL cotton paper at dew point 55.5°C, 80°C @ 32% RH, 70°C @ 50% RH and 60°C @ 80% RH, aged for 0–1372 days; note the parallel behavior in the later stages of this aging period.

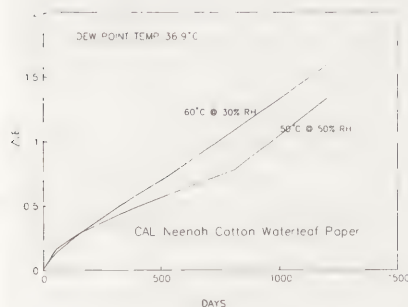


Figure 10. ΔE for the CAL cotton paper at dew point 36.9°C, 60°C @ 30% RH and 50°C @ 50% RH, aged for 0–1203 days; note the parallel behavior in the later stages of this aging period.

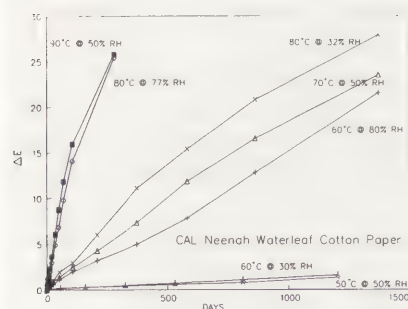


Figure 11. ΔE of all the dew point groups (74.0°C, 55.5°C and 36.9°C) for the CAL cotton paper; note distinct grouping by dew point and similarity to Whatman #1 filter paper data.

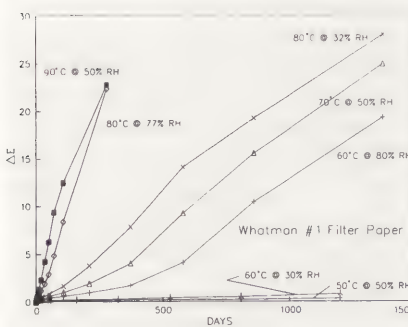


Figure 12. ΔE of all dew point groups (74.0°C, 55.5°C and 36.9°C) for the Whatman #1 filter paper. Note the grouping by dew point.

Table II. ΔE before (aged) and after washing, difference and percent difference of selected CAL cotton paper samples.

Series	Days of aging	ΔE aged	ΔE washed	Difference	Percent change
90°C@50%RH	0	0	0.19	0.2	NA
	69	11.74	9.34	2.4	21%
	278	25.79	23.94	1.8	7%
80°C@77%RH	69	9.75	7.90	1.9	19%
	278	25.42	24.45	1.1	4%
80°C@32%RH	373	11.10	7.31	3.8	34%
	581	15.38	12.06	3.4	22%
	861	20.80	17.23	3.6	17%
70°C@50%RH	373	7.32	4.44	2.9	39%
	581	11.84	8.16	3.7	31%
	861	16.55	13.40	3.2	19%
60°C@80%RH	373	4.96	3.43	1.5	31%
	581	7.81	5.49	2.3	30%
	861	12.80	10.90	1.9	15%
60°C@30%RH	1203	1.59	0.72	0.9	55%
50°C@50%RH	1203	1.34	0.68	0.7	49%

(2.9 units vs 1.75 units). The 80°C@32%RH and 70°C@50%RH changes range from 2.9 to 3.8 units and those for the 60°C@80%RH group range from 1.5 to 2.3 units. These amounts are larger percentages of the original color change than for the 74.0°C dew point group. This is so, even when samples that experienced about the same degree of color change are compared.

Figure 15 shows that for the 36.9°C dew point samples, about half of the color change is reversed by washing. Since the total color change in these samples is much smaller (1.5 vs. 5–25 units) than in the other groups the results cannot be compared directly.

Figures 16 and 17 show the spectral reflectance, 375–750 nm, data for selected samples before and after washing. Change occurs primarily in the yellow region.

Production of color

Color changes in both types of paper depend on time, temperature and relative humidity. Plots of the total color change, ΔE , are remarkably linear during much of the aging process. The shape of many ΔE plots exhibits an S-shaped curve typical of the deterioration of organic materials, as described by Feller¹⁹. In some plots, within the first few days a very fast but short-lived deterioration, inception period, can be observed. This is followed by a relatively slow induction period. A period of rapid increase after induction demonstrates an autocatalytic type of behavior. Prolonged steady state behavior, the linear portion of the curve, follows. None of the curves reached a termination point, but most show the declining rate indicative of autoretardation.

Deviations from linearity occur during the initial stages and after long periods of aging. The early stages of the plots for the Whatman #1 55.5°C dew point series are typical of autocatalytic behavior (an increasing slope followed by a steady rate), and the later stages of the plots for the 74.0°C dew point series are typical of autoretarded behavior (a slope that decreases over time). The non-linearity during the initial stages of aging can be due either to the effects of reactions that occur only during this period or because the amounts of intermediate reaction products had not yet built up to equilibrium (steady state) concentrations. The decrease in rate during the later stages of aging can be due to either the color of the paper approaching a limiting value or to the decrease of reactants that generate the colored products.

The complexity and variability of the ΔE curves, along with the appearance of some humps and features in the visible light reflected spectra and disappearance of others during aging, indicate that the production of color is not a single

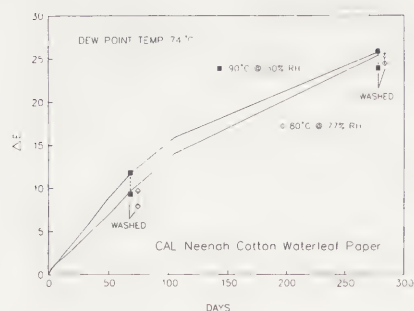


Figure 13. ΔE for the deionized water washed CAL cotton paper specimens following aging at 90°C @ 50% RH and 80°C @ 77% RH, for 69 and 278 days respectively, superimposed over the aged (only) data. Note that longer aging results in decreased loss of color as a result of washing.

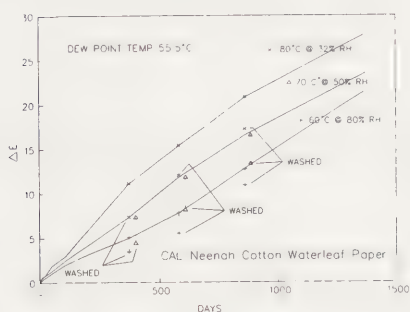


Figure 14. ΔE for the deionized water washed CAL cotton paper specimens following aging at 80°C @ 32% RH, 70°C @ 50% RH and 60°C @ 80% RH for 373, 581 and 861 days respectively, superimposed over the aged (only) data.

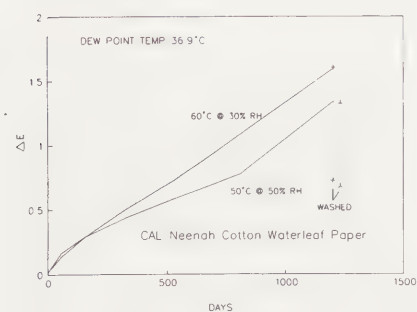


Figure 15. ΔE for the deionized water washed CAL cotton paper specimens following aging at 60°C @ 30% RH and 50°C @ 50% RH, for 1230 days respectively, superimposed over the aged (only) data.

reaction or process. This is confirmed by the fact that changing the temperature and changing the relative humidity affects the shapes of the curves differently.

Color change and deterioration reactions

While this report does not contain the results of degradation by-product analysis (in process) some preliminary conclusions can be drawn. The presence of water plays a large part in the development of color as indicated by the fact that an increase in relative humidity has a significant effect on the rate of color production. In going from 30–80% RH at 60°C, both the moisture content of the paper and the water vapor concentration in air increase 2.7 times while the equilibrium reaction rate increases about 14-fold. Going from 32–77% RH at 80°C increases the moisture content of the paper and the water vapor concentration of the air by roughly the same factor, 2.4 times, but this results in only a 6-fold increase in rate. Both of these values are greater than would be expected based upon a linear dependence of the reaction rate on either relative humidity or moisture content, i.e., a 2.4-fold to 2.7-fold increase in rate. The larger relative increase in the reaction rate at the lower temperature indicates that the overall process of color change is more dependent on water content at lower temperatures.

Changing the temperature from 50°C to 90°C at constant relative humidity (50%) produces a 120-fold increase in the rate of color production. Changing the temperature from 70°C to 90°C at 50% RH produces a 9-fold increase in rate.

Increases in relative humidity and temperature result in greater color production, but a smaller percentage of that color can be removed by washing. The amount of color removed by washing for samples with a ΔE of about 10–11 is halved (3.8 vs. 1.9) for the increase in relative humidity from 32% RH to 77% RH at 80°C. For an increase in temperature from 70–90°C at 50% RH, the amount of color removed by washing (for samples with a ΔE of about 12) decreases by about one third (3.7 to 2.4).

Application to storage

The most striking feature of the graphs is the clustering of the curves into three distinct groups based on the dew point of the air flowing through the chambers. The curves within each of the three groups differ from each other by less than they differ from curves of other groups. This is the combined result of two opposing effects. If the temperature is raised at constant dew point then the relative humidity decreases. These two changes (higher temperature, lower relative humidity) produce opposing effects.

An increased temperature means that all molecules of the reactants have a greater average energy, and specifically that a higher proportion of them have the amount of energy necessary for a reaction to occur. Raising the temperature at constant relative humidity should increase the rate of all reactions that are occurring. This can be seen by comparing pairs of curves with different temperatures but the same relative humidity, e.g., 60°C@80%RH and 80°C@77%RH; the 80°C@77%RH conditions result in an increase in the rate of production of color.

Relative humidity is directly related to the activity (effective concentration) of water. A relative humidity of 100% is the equilibrium water vapor concentration over liquid water. A relative humidity below 100% thus represents the water vapor concentration over a liquid with an "equivalent" concentration of water, i.e., 50% water in alcohol solution. Thus one finds, for instance, that the amount of water vapor absorbed in paper is directly related to relative humidity rather than to the absolute water vapor concentration of air. There is 5.7 times as much water vapor in the air at 90°C@50%RH than there is at 50°C@50%RH, but the amount of absorbed water in paper is approximately the same, only 1.15 times greater at 90°C than at 50°C at 50% RH²⁰. Lowering the relative humidity at constant temperature reduces the amount of water absorbed in paper. Less water results in reduced rates of those reactions which are dependent upon water. The effect of lowering the relative humidity can be seen by comparing the

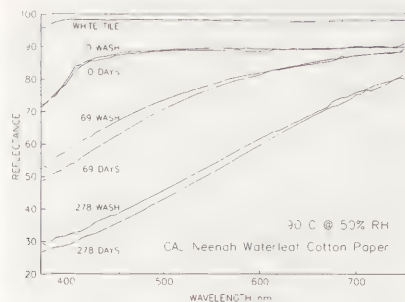


Figure 16. Reflectance spectra, 375–750 nm, for the CAL cotton paper specimens which were washed in deionized water following aging at 90°C @ 50% RH for 69 and 278 days respectively, with the HunterLab white tile reference standard.

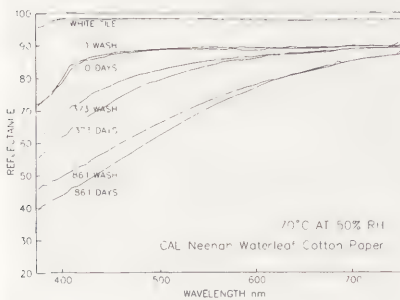


Figure 17. Reflectance spectra, 375–750 nm, for the CAL cotton paper specimens which were washed in deionized water following aging at 70°C @ 50% RH for 373 and 861 days respectively, with the HunterLab white tile reference standard.

80°C@77%RH curve with the 80°C@32%RH curve. Lowering the relative humidity to 32% decreases moisture content of the paper from 7.0% to 2.9%, to 40% of its 77% RH value, while the rate of reaction decreases to less than 20% of its value at 77% RH²¹. Thus, the reaction rate decreases with the decreases in RH and moisture content, though the relationship is not linear.

If the dew point is kept constant as the temperature is raised, then the relative humidity is lowered. This occurs in the change from 60°C@80%RH to 80°C@32%RH. Increasing the temperature tends to increase the rates of all reactions, but the lower relative humidity tends to decrease the rate of water dependent reactions. It turns out that for color change these two effects nearly cancel each other out. Thus the plots within each of the three groups are similar. This, of course, is only because the relationships between the rate of color change and the temperature and relative humidity are such that the increase due to the increased temperature and the decrease due to the decreased relative humidity happen to be about the same. Larger differences would be obtained in a system in which the degradation process had a different degree of dependence on the temperature or relative humidity. A reaction in which water played no part, for instance, would have the same rate at different relative humidities if the temperature were held constant, and would speed up with increased temperature no matter what the relative humidity.

Color change for these samples can be relatively accurately predicted (especially the slopes of the linear portions of the plots) within the range of conditions studied from the *dew point only*, without knowing either the temperature or relative humidity. For instance, the 70°C@50%RH curve would provide a relatively accurate prediction of color change for any of the aging conditions with a dew point of 55.5°C. Knowing only the temperature or the relative humidity does not allow such accurate predictions.

If, and this is by no means certain, such results are found to extend to other aspects of the aging of paper, such as other chemical reactions and mechanical and physical properties, then the implications for the storage of paper are profound. Fifty percent relative humidity is widely recommended and maintained in many museums, archives, and libraries. Chemical considerations argue for a lower relative humidity to reduce the rate of the water dependent aging processes. Physical and mechanical considerations argue for higher values of relative humidity to prevent damage caused by the fact that paper is stiffer and more brittle at lower relative humidities. Building engineering HVAC (heating, ventilation, and air conditioning) considerations place a limit on the dew point temperature (somewhere above freezing) that can be maintained within a conventional building (not a cold storage facility). To minimize color change (and possibly other types of chemical degradation), a higher priority should be placed on maintaining a low dew point rather than a specific relative humidity. Once the dew point is chosen then the temperature can be adjusted up or down to achieve a relative humidity that is acceptable based on physical considerations such as stiffness or brittleness, and other considerations such as human comfort.

These results indicate that a low dew point minimizes color change. Further work on the chemical and physical changes that have occurred in these paper samples is planned and should help to determine whether the conclusions derived from the color change results also apply to other degradation processes.

Effects of washing

The washing data demonstrate that the amount of soluble material contributing to color change varies with the degree of deterioration and the conditions that cause it. Samples with greater deterioration (higher ΔE) lose a lower proportion of acquired color than samples with less deterioration. The darker the color prior to washing, the smaller the percent color change that results from washing.

Samples that have been aged under different conditions which seem to have experienced the same "amount" of color change as indicated by similar values of ΔE contain different proportions of soluble colored material indicating that they have aged "differently." For example, in samples with a ΔE of about 12,

washing removed 2.4 ΔE units of the color in the 90°C@50%RH, 69 days sample while in the 80°C@32%RH, 373 days and 70°C@50%RH, 581 days samples the loss was 3.7–3.8 ΔE units; about 50% more color lost in the lower dewpoint samples.

Conclusions

- Color changes occur in both types of paper, and the rate of change varies with the conditions of temperature and relative humidity. Plots of the total color change, ΔE , are remarkably linear in the middle stages of color production. Many ΔE plots exhibit an S-shaped curve typical of the deterioration of organic materials.
- The production of color during artificial aging has a complex mechanism, which consists of more than one reaction and is dependent upon a number of environmental factors.
- Dew point is the best predictor of the rate of color production.
- An increase in temperature from 50°C to 90°C causes a 120-fold increase in the equilibrium rate of color production.
- An increase in relative humidity from 30% to 80% (at 60°C or 80°C) results in a 6-fold to 14-fold increase in the equilibrium rate of color production.
- When washed, samples with greater color do not lose the same proportion of acquired color as samples with less deterioration; darker samples lose less color. It appears to be desirable to wash paper with small amounts of color change, as well as those which are regularly considered for such treatment.
- In selecting storage conditions to *minimize color change*, a higher priority should be placed on choosing the lowest possible dew point rather than a specific temperature or relative humidity.

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Abstract

An unknown mediaeval treatise on the techniques of manuscript illumination is discussed. Its relation with the Strasbourg manuscript is pointed out, and the use of a particular type of colorant in both manuscripts is studied. The possibility of identification of anthocyanin colorants by chromatographic and spectrophotometric techniques is discussed.

Keywords

Leiden manuscript, Strasbourg manuscript, illuminations, anthocyanins, clothlet, spectrophotometry, chromatography

Natural Organic Colorants on Mediaeval Parchment: Anthocyanins

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Introduction

In the scientific study of painted art objects such as miniatures, paintings, and polychrome sculptures, a wide and ever expanding knowledge has been gathered on inorganic colorants. Much less attention is usually given to colorants of organic origin. These colorants, however, are usually the most vulnerable. Organic colorants are the first to change with fluctuations in temperature and relative humidity. More than mineral pigments, they change color on the slightest changes in pH. They rapidly fade in ordinary daylight. In short: from the point of view of conservation of cultural property, organic colorants deserve wider attention than they have had thus far.

Many historically used organic colorants were derived from plants. In plants, organic colorants usually occur in combination with a large number of other vacuolar constituents, such as other colorants, mineral ions, sugars, peptides, and organic acids. Most dyestuffs that were to be applied in art objects are, in their natural state, customarily linked to sugars. The extraction procedure usually involved the breaking of these sugar bonds, often by enzymatic hydrolysis. The second step was to establish new bonds between the aglycon, i.e. the colorant without its sugars, and the fiber or substrate by metal complexation. Of the mordants used for complexing the aglycon colorants, metal salts containing aluminum, potassium, calcium, magnesium, tin, copper, and iron are the most important.

For mediaeval panel paintings or manuscript illuminations, colorants based on quinoid or flavonoid compounds were extracted by warming the plant materials in soft lye solutions. Then the plant material was removed by filtration. The colorant in the lye—usually potassium or sodium carbonates—remained. Upon addition of a warm aluminum sulfate solution to this extract, a dense aluminum hydroxide precipitate would be produced that formed highly stable and color enhancing bonds with the colorants. Other colorants were used without aluminum hydroxide complexation. These colorants, usually applied as "clothlet" colors, were often anthocyanin colorants from plants.

The Leiden manuscript, a treatise on illumination

Descriptions of the use of these anthocyanins on parchment can be found in a hitherto unpublished 15th century manuscript treatise. This workshop handbook primarily gives recipes for the use of these anthocyanins in the form of clothlet colors. The manuscript in the Leiden University library has the shelf mark "Cod. Voss. Chym. Oct. 6." On the inside of the cover the contents of the manuscript is described: "Methodus aquae conficiendae ad temperandos omnes colores, & sic procedit ad quaecunque alia sive remedia, sive oblectamenta tincturarum, privato labore collecta. Germanice & Latine." From the contents of the texts it is evident that this is not a general technical treatise but is specifically written for the use in the workshop of a penman or manuscript illuminator. The recipes pertain to the making of inks, the best way to mix the red ink of the rubricator, the use for penwork of various natural organic colorants, and the various ways gold leaves were to be applied in illuminations.

What makes this manuscript so special is the fact that it appeared to be closely related to the famous "Strasbourg manuscript." A transcript of the Strasbourg manuscript was published in 1897 by Ernst Berger after a 50-year old copy by Sir Charles Lock Eastlake (1). The original Strasbourg manuscript itself had gone lost during the fire of the Strasbourg University Library in 1870. Berger called it the "älteste deutsche Quelle für Maltechnik." And indeed, for a long

time the Strasbourg manuscript has been considered the oldest and foremost art technical treatise in a Germanic language. And it was considered to be without predecessors or later copies.

Later studies by Rockinger, and especially by Ploss, showed that there are certainly other manuscript texts (or fragments thereof) that show relationships with the Strasbourg manuscript (2, 3). These relationships may vary from almost the complete text to only single recipes. Of the recipes or collections of them that have hitherto been published, the Leiden manuscript seems to be the one closest related to the Strasbourg manuscript. A good example may be shown by comparison of a particular line where a context error in all related texts can be found. The Amberger Malerbuch (Cod 77) says on fol. 222r: “. . . werd der plumen saff ein quertlein so gehort ein settich aluminis darzw wer aber der plumen nicht alz vil, so leg mit not dar in vber daz settich d[] alvn gar dar ein chomen . . .” The same line appears in the early 16th century Tegernsee manuscript (Cgm 821) on fol. 30v as: “. . . Wär aber der plumen saff ain quertlein, so gehort ain seitti alawn darein. Wär aber des saff nit so vil, so leg mit not dar ein vber das settit alawn gar dar ein komen . . .” Berger’s edition of Eastlake’s copy reads: “. . . werde der blumen ein quertelin, so gehort denn ein settit dar in alans, wer aber der blumen nüt also vil so lege nüt not dar an und ob das settit alans genot dar in keme . . .” (4). The same line in the Leiden manuscript is on fol. 17v.: “. . . werde der blumen ein quertlin so gehort ein settich aluns dar in were aber der blumen nit vil so leg nüt not dar an und ob das settich aluns gar dar in keme . . .”

Since the source on which Ernst Bergrers publication was based, was only a copy of the original, the finding of this Leiden manuscript may be of great significance for our understanding of the transmission of mediaeval paint technology and for the study of the original text complex.

Leiden	Strasbourg
1	23
2	24
3	12
19	13
22	17
23	18
25	19
26	20
27	21
29–30	22
31	25
32	26
33	27
34	28
35	29
36–37	30

To facilitate a better understanding of the relations between the Leiden manuscript and the Strasbourg manuscript as copied by Eastlake, a concordance of recipes is shown in Figure 1. In this concordance the recipes listed under Leiden are numbered by the author. The recipes under Strasbourg are rendered according to their numbering in Berger’s edition. The recipes in this concordance show literal similarities. Other recipes may show textual similarities but have differences in prescribed quantities or binding media. The Leiden manuscript has some additional recipes, some of them on the coloring of parchment that are missing in the Strasbourg copy.

The Strasbourg manuscript got its name from the city in whose library it was kept before it got lost as result of war casualties. There is no reason to assume that it came from any other than the Strasbourg geographical area. There seems to have been a certain relation of the manuscript with the ordinances of the Strasbourg painters’ guilds of 1456 (5).

In the Strasbourg manuscript, mention is made of the manner of painting as practiced by the master Andreas of Colmar and master Heinrich of Lübege (6). Moreover, Berger has found that several recipes in the Strasbourg manuscript could be found back in the Valentinus Boltz recipe book for book illumination. Valentinus Boltz, whose book with the title: *Illuminier Buch, wie man allerley farben bereiten, mischen, schattieren, unnd ufftragen soll*, appeared in 1549 in Basel, came himself from Ruffach in the Alsace area. Reference in the Leiden manuscript to certain measures of volume, “gummy arabicum als gross als ein walsche -Walonian-erwis” (ms fol. 4v), to regional quality grades: “lusch -Liege- gel” (ms fol. 7v), “pellicarie das ist crid die die luicssner—people from Liege—hand” (ms fol. 8v), “oger von Metz” (ms fol. 11v), as well as linguistic characteristics and the watermark of the paper, give strong indication that this manuscript is also from that area (7).

Since these three sources seem to have a sound provenance from the Alsace-Lorraine area, it is safe to assume that the contents of the recipes in the “Strasbourg” complex represent the current practice of manuscript illumination in that area. One of the more prominent characteristics of the miniatures made in

Figure 1. Recipes under Strasbourg rendered according to their numbering in Berger’s edition.

Alsace in the mid-15th century is the lavish use of transparent washes with organic colorants over inorganic pigments.

And it is precisely in the descriptions of a large variety of wash colours in the form of clothlets, that the manuscripts of the "Strasbourg"-group distinguish themselves from common mediaeval workshop practice. The traditional, mediaeval practice of manuscript illumination was to work in superimposed layers of opaque paint. Usually the figure to be painted was drawn in ink. The figure was then painted in one single paint layer in a uniform colour. Next on the shadow side of the figure the contours were drawn and some shadow was indicated by a darker paint tone in opaque hatching: the *incidis*. Then the figure was raised on the light side by the application of light hatching and the addition of a thin light contour line: the *matizatura*. Each colour or pigment had its own set of prescribed *incidis* and *matizatura* colours. In this procedure a relatively large number of steps is involved to come to the final result (8).

The water colour procedure as adopted in the 15th century made it possible to produce the illuminations at a much faster pace. After the initial drawing was made, and the base colours were laid, it was usually sufficient to work the modeling of the figures in just a few rapid washes in water colour. These water colours were made on the basis of a large variety of plants sources.

The Leiden manuscript gives in recipe 5 a blue ink: "tzu corperieren" a description for the preparation of an opaque paint with azurite. The following recipe 6, however, mentions a blue ink: "tzu floreren" (i.e., to flourish) with a clothlet colour. Recipe 7 simply states that to make "violvarw" (i.e., a purple colour), one should take the purple clothlet and proceed as with the blue clothlet.

Recipe 31 describes under the heading: "Blau tornisol. Wiltu machen schon fin tuchlin blaü varwe . . .", how this blue clothlet is made. For the blue, twelve hands full of corn flowers ("korn blumen") were collected within eight days after Whitsuntide. The flower petals were treated in a mortar into a pulp. The pulp was packed into a clean cloth which was then pressed out. In the juice of the petals that thus was gathered, a small amount of ammonium chloride ("salis armoniaci") was dissolved. Then clean linen cloths were steeped into the plant juice and after they had taken enough of the colorant, they were hung to dry in a shady place. The next day the whole procedure was repeated but this time the juice of the flowers was treated with gum arabic and alum ("alumen glarici"), before the same cloths were seeped again in the juice of the petals. After the cloths were thoroughly dried they were wrapped up in paper and carefully stored away from any humidity ("setze es bor an den luft das es nit fucht habe"). A similar procedure was followed for violet clothlets with red cornflowers ("rot kornblumen") and for purple clothlets with blueberries ("heydelber").

It is obvious that all these clothlets, although they were all called "tornisol" (i.e., turnsole) in the manuscript have nothing to do with the real turnsole, which is derived from the Mediterranean plant *Chrozophora tinctoria* Juss (9). Instead, it seems reasonable to assume that manuscript illuminators used plant colorants that were locally available. It seems likely that blue cornflowers (*Centaurea cyanus* L.) can be taken for the manuscripts "kornblumen." Similarly the manuscripts "rot kornblumen" can be translated as poppy flowers (*Papaver rhoeas* L.) and "heydelber safft" is the juice of blueberries (*Vaccinium myrtillus*). Other sources also seem to have been used. Berger called the "roten blumen", for a purple clothlet, in his edition of the Strasbourg manuscript as a certain ranuncle: *Paeonia officinalis* L. Also the use of elderberries (*Sambucus niger* L.) for clothlets seems to have been fairly common. These clothlets all have anthocyanins in common as their colouring principle.

Anthocyanin colorants

The anthocyanins are pigment glycosides that are responsible for most of the red, blue or violet colors in the flowers of higher plants. The aglycons, i.e. the colorants without their natural sugars, are called anthocyanidins. The names of

the most frequent anthocyanidins stem from the names of the plants in which they occur, or in which they were detected for the first time.

<u>Anthocyanidin</u>	<u>First presence established in</u>
pelargonidin	<i>Pelargonium zonale</i>
cyanidin	<i>Centaurea cyanus</i>
peonidin	Peony (<i>Ranunculaceae</i>)
delphinidin	<i>Delphinium consolida</i>
petunidin	<i>Petunia</i> spp. (<i>Solanaceae</i>)
malvidin	<i>Malva sylvestris</i>

Anthocyanidins other than these six are rare. The three most common pigments (pelargonidin, cyanidin, and delphinidin) differ in structure only by the number of their hydroxyl groups. They provide, either singly or as mixtures, the whole range of flower colour from pink and orange to violet and blue. Broadly speaking, all pink scarlet and orange-red flowers have pelargonidin, all crimson and magenta flowers have cyanidin, and mauve and blue flowers have delphinidin (10).

The anthocyanins do not form a specific group but are part of the larger group of the flavonoids. They differ from most other flavonoids through the presence of a basic oxygen atom. Unlike most other flavonoids the anthocyanidins cannot be easily be laked into insoluble pigments by complexing with mineral ions.

Anthocyanins have the same basic skeleton as the other flavonoids, which is based on the association of two products, each of them coming from a different biosynthetic route. In the anthocyanins the B-ring probably is hydroxylized after the formation of the C₆-C₃-C₆ skeleton. Anthocyanins possibly occur *in vivo* as salts from weak organic acids. The differences in colour of the anthocyanins, usually blue, red or purple, are basically caused by substitution at the B-ring. Most aglycons have hydroxyl groups at the 3, 5, and occasionally at the 7 positions. The B-ring can have substitutes on 3', 4' and 5' positions. The differences in colour are determined by the structure of the colorant as well as by the positions and numbers of attached hydroxy-, and methoxy groups.

Sugars attached to the anthocyanins may occur as monosides, biosides, and trioside. As 3-monosides they usually occur as 3-glucosides or 3-galactosides, as 3-rhamnosides and 3-arabinosides they are rare. Biosides, i.e., sugars built up of two mono-saccharides usually are 3-rhamnossylglucosides. As the name indicates, this sugar group is composed of rhamnose and glucose, and is also called rutinose. The triosides all have their sugar rest attached to the 3 position. The ones built up of three glucose units, gentiotriosides, have a linear structure. Trioside combinations of rhamnose and glucose, xylosylrutinose, have a branched structure.

Anthocyanins and anthocyanidins are not stable in water. They are highly subject to proton transfer reactions. Therefore the warning in the Leiden and Strasbourg manuscripts that the clothlets be stored as dry as possible certainly makes sense. Substituted anthocyanidins are more stable against these reactions. Therefore their reaction with sugars of the gum arabic when the cloths were soaked in the petal juice or with the prescribed ammonium and aluminium salts may have contributed to the preservation of the colour during storage.

There is a fairly large variation in the different compositions of the anthocyanin-based clothlet colours. The cyanidins in a particular type of myrtle berries (*Vaccinia angustifolium*) are found to consist of a very complex mixture of 3-galactosides, 3-arabinosides and 3-glucosides of cyanidin, peonidin, delphinidin, petunidin, and malvidin. The more ordinary myrtle berry (*Vaccinia myrtillus*), which most likely was the type of berry known to the writer of the Leiden manuscript, are found to contain arabinose and glucose derivatives of cyanidin, delphinidin, petunidin and malvidin. The cyanidins in the fruit of elderberry (*Sambucus nigra*) are mainly composed of 3-sambubiosides and 3-glucosides. Cyanidin 3-sophoroside and pelargonidin 3-sophoroside are known to occur widely in *Papaver* spp. Also, 3,5-diglucosides of cyanidin can be found in *Centaurea cyanus*.

Anthocyanins on parchment

The use of natural organic colorants without previous metal complexation into pigment lakes has led to the association with contemporary textile dyeing. Mediaeval paper was made out of pulp of linen fibers. The adherence of the colorant to the manuscript leaves was thought to be caused by the staining of the paper fibers, in a similar way as it had stained the clothlet. The illuminator was not really painting, but rather staining the fibers: "... müsste man eigentlich von einem Faerben der Leinenpapiere sprechen" (11). Ploss inferred from this analogy that recipes describing clothlet colours were typical only for the later middle ages when the use of linen pulp paper became general practice. And clothlet colours would not be suitable for application on parchment. There are a number of arguments against this position.

There is a large number of recipes describing the use of clothlet colours, and the use of other not-complexed natural organic colorants, dating from before the introduction of paper in western Europe.

Wherever a carrier is mentioned in the Leiden manuscript it is about parchment. Recipe 15 says: "Wiltu apprement temperieren . . ." Recipe 20: "... schrib uff das bermit . . ." and recipe 21 states that: "man sol das berment wol prunieren."

In fact, the description of paper in the Leiden manuscript limits itself, with one exception, to the use of it as packing material for clothlets. This particular exception is recipe 44: "Wiltu machen ein bulver so man ez uff bappir oder uff bermit lut . . .", where a staunch grain, made of mastic and egg shells, is described. This powder was to make paper as well as parchment less absorbent, so that writing on it would be easier.

The last part of the Leiden manuscript, running from recipe 37 to recipe 46 has recipes that do not occur in the Strasbourg manuscript. Some of them deal with the coloring of parchment and explicitly mention the use of clothlet colours for it. Recipe 38 says: "Wiltu das bermit blu verwen. So netz es in tuchlin blau ein nacht" (If you wish to stain the parchment blue. Soak it in clothlet blue during one night). And in recipe 39: "Wiltu es violvarw verwen so netz es in heydelber safft ein nacht" (If you want to stain it blue, soak it in blueberry juice). There can be no doubt that the juice of the petals that was used for the making of the clothlets and the juice applied in the dyeing of parchment leaves were the same. And also the other organic colours that had a previous description in the manuscripts' recipes to make water colours, appear as source for staining whole parchment leaves. It appears from the Leiden manuscript's recipes that clothlet colours were used to stain parchment rather than paper, and that it was also on parchment that transparent washes of clothlet colours were used.

It is in particular this technique of using thin wash colours made of organic colorants that should be taken into account when we examine the recipes of the "Strasbourg"-complex. Some of these recipes describe how to "molen und ouch ze florieren nach lamptenschen sitten" (to paint and flourish in the "lamptenschen" manner). In his comments on the Strasbourg manuscript, Eastlake concluded that this "lamptenschen sitten" referred to the London practice of painting (12). This opinion was shared by V. and R. Borrodaile in their edition of the Strasbourg manuscript (13). At that time, however, there was no particular specific technical difference that would set the London practice apart from what was common in the rest of Europe.

With respect to the use of organic colorants, it is to be noted that usually the techniques described in technical treatises do not significantly differ from what was common in that place or time. However, in the case of the watercolour animals in the "Carnets lombards" made in northern Italy, we are confronted with an innovation. It was likely in that region that draughtsmen first came to realize that the tools of their trade offered unique possibilities to represent not just various textures in silver point, but also gradual transitions in shades and tonalities by laying thin washes. This watercolour method as distinguished from the traditional miniaturists use of opaque colours in *incidis* and *matizatura*, could produce a hitherto unknown degree of plasticity. A good example can be found in the book of hours of the Master of the Hours of Isabella of Castille (14).

Many of the illuminations in his manuscript are done in the traditional opaque technique. However, some of the beautifully modeled, gracious animal figures appear to be directly derived from models as the ones in Giovannino dei Grassi's modelbook in Bergamo (15). It is important to note that here, as in almost all other Lombard model books of the time, the wash drawings were executed on parchment. It was especially in the Lombard manuscript illumination, and more specifically in the "Carnet lombards" that we see an increased use of transparent wash colours.

Paecht, Wormald, and Scheller all described the use of transparent water colours in northern European parchment manuscripts as the result of Lombard influence. In the 15th century the influence of Giovannino dei Grassi and Belbello da Pavia was notable (16). It seems reasonable to assume that the expression "Lampertschen sitten" refers to the use anthocyanin-based water colours.

Analysis

For the analysis of anthocyanins on works of art, either chromatographic or spectrometric techniques can be used. Analyses should be based on comparison with standards.

Chromatography

The standards for anthocyanins are not commercially available, but have to be extracted from the plant sources. Isolation of anthocyanidins is done by hydrolysis. After hydrolysis, the cooled liquid must be washed twice with ethyl acetate in order to remove any eventual flavones from the extract. The liquid phase must then be heated for 3 minutes at 80°C to remove any residues of the ethyl acetate. The anthocyanin-colorant can then be extracted out with a little bit of amyl alcohol. The amyl alcohol-extract can now be concentrated on a hot water bath and taken up with methanolic HCl for chromatography.

In attempts to isolate the colorants, special precautions must be taken. The anthocyanins, as well as their aglycons, are unstable in neutral or alkaline solutions. Under the influence of light the colour may disappear in acidic solutions. If for the making of standards, larger amounts of anthocyanidins are made by preparative column chromatography, the column must be covered because the aglycons rapidly decompose in ambient light. The colorant still is best extracted from the plant in methanolic HCl (0.01%), and dried in vacuo. Hydrolysis is usually done in 1 N HCl at 100°C. Most 3-glucosides and 3-galactosides will be completely hydrolyzed after thirty minutes, whereas it will usually take one hour to hydrolyze the triglycosides and transform them into their aglycons.

The best stationary phases are either paper or cellulose plates. Silica gel plates are less favorable because they do not seem to give a good separation of the colorants. Cellulose plates, however, offer good separations, but their capacity, compared to that of paper, is not excessive.

Often used eluents are BAW (n-Butanol:CH₃COOH:H₂O, 4:1:5), or BuHCl (n-Butanol:2 N HCl, 1:1), or a 1% solution of HCl in water. For identification of anthocyanidins, (after hydrolysis of anthocyanins in 1 N HCl at 100°C for 40 minutes) mixtures such as Forestal (conc. HCl:CH₃COOH:H₂O, 3:30:10) or Formic (conc. HCl:HCOOH:H₂O, 2:5:3) have also frequently been used.

The combination of the R_f-values in various mobile phases may give sufficient information on the identity of certain components. In general it can be said that the most determining factor for R_f-values is the number and nature of sugar rests. Other determining factors are the polarity of the molecule and the substitution at the B-ring. Increase in glycosylation will result in lower R_f-values in a-polar mobile phases and higher R_f-values in more polar eluents. This is due to the fact that by glycosylation the polarity of the molecule increases. Thus diglycosides have stronger elution than monoglycosides. The monoglycosides on their turn have a faster transport on plate or column than their aglycons. The importance of B-ring substitution is best demonstrated by the fact that delphinidin has a more rapid transport than cyanidin. Cyanidin has a shorter

	I	II
<i>Papaver rhoeas</i>		
pelargonidin 3-sophoroside	36	30
cyanidin-3-sophoroside	33	22
<i>Sambucus nigra</i>		
cyanidin-3-sambubioside	36	24
5-glucoside	19	10
<i>Centaurea cyanus</i>		
cyanidin-3,5-diglucoside	28	06
<i>Vaccinia</i> berries		
peonidin-3-arabinoside	48	42
3-galactoside	39	28
petunidin-3-galactosides	33	13
malvidin-3-galactosides	36	15

Figure 2. Rf values on cellulose plates of some anthocyanins, most commonly occurring in clothlets. Data as published by Harborne, Comparative Biochemistry of the Flavonoids, London 1967, pp. 30–36. Solvent I is a mixture of n-butanol:acetic acid:water (4:1:5). Solvent II is a mixture of n-butanol:2 N HCl (1:1).

retention time than pelargonidin and peonidin. The phenolic hydroxy-group is more polar than the methoxy-group.

Analytical chromatography should always be done with reference standards. Thus the theoretically established Rf-values can be compared with experimental results of reference standards. The colours of the spots on plates tend to disappear more rapidly than those on paper, and therefore should be marked immediately. Identification of the spots can be done in ambient and ultraviolet light. Distinctive colour changes can be made by changes in pH and formation of iron (III)-complexes (17). The use of thin-layer chromatography (TLC) is limited by the size of the sample that can be taken from the art object. A good alternative for analytical (TLC) would be high-performance liquid chromatography (HPLC) with diode array detection or, in the case of extremely small samples, HPLC with detection and measurement of different fractions in the fluorescence spectrometer (18).

Spectrophotometry

The spectral characteristics of the anthocyanins also allow for identification by UV-visible absorption spectrometry (19). The most convenient solvent for spectral determinations is methanol containing 0.01% conc. HCl. The glycosides have two maxima, one in the lower wavelength region around 275 nm and one in the visible range between 465 and 550 nm. The maxima in the higher wavelength ranges are mainly dependent on the hydroxylation patterns of the aglycons, rather than on the nature of the sugar substituents. The 3- and 3,5-diglycosides both have almost the same absorption maxima. These glycosides can be distinguished by determining the relation between the maximal absorptions in the visible region and in the ultraviolet.

Absorption spectrometry should preferably be done with solutions of relatively pure substances, rather than closely related mixtures. Because the maxima of the various pigments are in the same wavelength regions, there is a large possibility of overlapping peaks. In such a case, the absorbance at a certain wavelength consists of the absorption of one pigment that has its maximum at a certain point, combined with the absorption of a second pigment nearby. Special computation devices accounting for peak overlap, like subtraction techniques may be needed.

UV-vis absorption spectrometry is not the most useful technique for unambiguous identification of anthocyanins on works of art. Fluorescence spectrometry may prove to be a more useful tool in the identification of anthocyanin colorants. It has been shown that 3,5-diglycosides of pelargonidin, peonidin, rosadin, malvidin, and hirsutidine show strong fluorescence emission, whereas the 3,5-diglycosides of other anthocyanidins exhibit only weak fluorescence. Fluorescence spectrometry of anthocyanins is marked by three parameters, i.e. excitation

wavelength, emission wavelength and quantum efficiency. Fingerprints based on contour plots and three-dimensional representation may identify most clothlet colours in small samples.

Conclusions

Many colorants used in mediaeval manuscript illumination were organic dyes from plant sources. These colorants were often anthocyanin substances, applied as clothlet colours. Mediaeval technical treatises can often yield significant information on the preparation and the use of these colorants. Historical technical sources may be highly valuable instruments in the study of art and artistic techniques. They may equally be important in questions concerning the conservation of art objects. Art-technical treatises, therefore deserve to be more widely studied and published. A very interesting treatise, now in the Leiden University Library, gives useful information on the use of anthocyanin colorants in manuscript illumination (20). These anthocyanin dyes can be identified by chromatographic and spectrophotometric techniques.

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Abstract

The Codex Eycensis, an 8th-century illuminated manuscript on parchment, was freed from its polyvinyl chloride lamination, applied in 1957. Many single sheets and bifolios needed to be conserved, especially in the spine regions and on the edges. Rebinding could only be considered if bifolios and, hence, quires could be restored by soft mechanical means. Aqueous suspensions prepared from hide powder, combined with paper fibres or calcium carbonate, or preliminary suspensions derivatised with formaldehyde, were used to produce sheets of reconstituted parchment. These were tested for their physico-chemical properties (acidity and opacity) and mechanical properties (tensile, tear, and thread tear strength), also after ageing. A fragment of old degraded parchment was leafcast with formaldehyde-treated parchment pulp. The reconstituted parchment proved to be mechanically strong and to be rather weakly bound to the original parchment, unless the contact zone was covered with goldbeaters' skin. The mixtures finally selected contained only minor quantities of modifying agents (< 20% by weight) and proved to be valuable materials for parchment leafcasting.

Keywords

Parchment, hide powder, leafcasting, conservation, codices

Table I. Evaluation of the condition of the sheets of the Codex Eycensis and selection of the material to be used for their consolidation, implying reconstitution of bifolia.

	Total amount	Repair possible with parchment	Repair needed with pulp
Single folio	5	5	0
Bifolio (firm)	24	2	22
Bifolio (weak)	17	1	16
Separated folios	23	12	11

Parchment Leafcasting with Dermal Tissue Preparations

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Introduction

The possible application of dermal tissue preparations for parchment leafcasting was investigated within the framework of the conservation project for the Codex Eycensis, an illuminated manuscript on parchment from the 8th century A.D. The condition of the parchment was investigated previously and old laminations with synthetic membranes were removed (1). In another paper, the results of the following investigations were presented: the microbial contamination of the parchment, comparison of adhesives to be applied in the subsequent conservation, and the preparation and properties of goldbeaters' skin (2).

Many sheets of the codex were severely damaged, often in the spine areas. In several bifolia, the sheets were detached, leaving an open space where parchment material was clearly lacking (See table I and fig. 1). The degradation of the edges excluded any mechanical manipulation so that a softer method for the reconstitution of the lacking parchment had to be developed if rebinding of the quires would be the final conservation option.

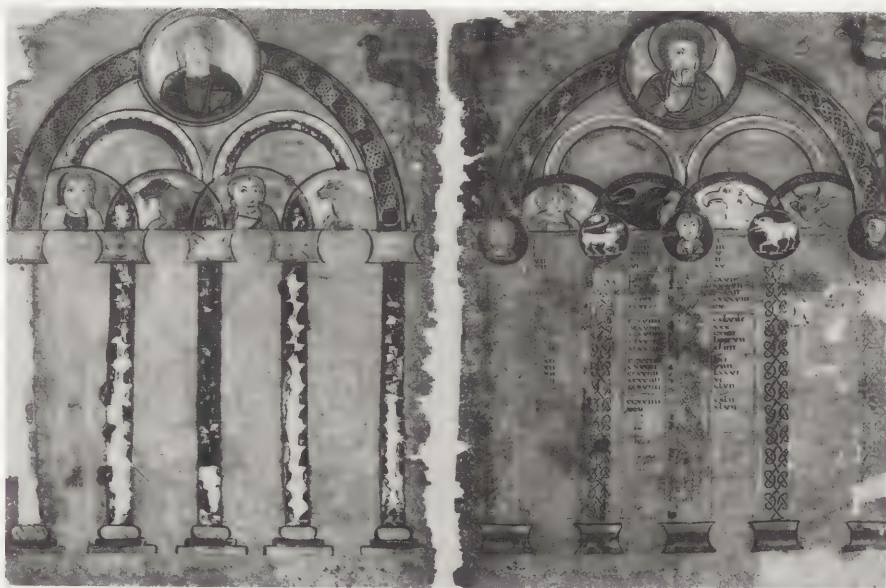


Figure 1. A bifolium, actually consisting of separated single folios. The relative position of the single folios reflects the way they will have to be combined in the new bifolio, implying the addition of material lacking in the zone of the fold.

After long discussions with conservators, codicologists, bookbinding specialists, and chemists, it was decided to rebind the codex for the following reasons: It was considered dangerous to keep available for display and consultation a manuscript in the form of different loose sheets. The building which housed the manuscript was not equipped as a museum and lacked a curator. It was necessary to consolidate the very fragile sheets to avoid losses caused by manipulation, so that the selection of an appropriate consolidant would probably allow rebinding

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as well. Finally, the presentation of the rebound codex would increase its value as a museum object to lay people. To reach these goals, it was decided to investigate the use of aqueous suspensions of dermal collagen for parchment repair.

Principles of parchment leafcasting

Parchment leafcasting has been described before, using dry parchment dust, paper pulp, or mixtures of paper and collagen fibres (3–5). Our approach to parchment leafcasting was outlined in a previous publication and mainly contained the following criteria: minimize additives other than collagen, limit the contact between water and the original parchment, and control the dimensional stability of added and old parchment (6).

In this paper, the following nomenclature will be used: “parchment pulp” for any suspension mainly containing collagen fibres originating from dermal material (i.e. hide, parchment); “reconstituted parchment” will indicate the solid deposit formed by the removal of liquid water from the parchment pulp on a porous filter plate.



Figure 2. Sheets of reconstituted parchment are formed by vacuum filtration of an aqueous suspension of dermal collagen fibres, eventually combined with other materials.

In a first series of experiments, samples of reconstituted parchment were prepared by filtering parchment pulp preparations through a funnel, provided with a 120 mm internal diameter sintered glass disk, and by applying a vacuum under the filtering disk (See fig. 2). For the study of applications in practice, reconstituted parchment was formed within the gaps of old parchment on a specially designed vacuum table, provided with a porous top plate, vacuum device, and illumination from beneath through the transparent bottom plate of the vacuum unit.

Reconstituted parchment was prepared according to the following recipe: Weigh the required amount of dry hide powder and add an appropriate volume of 0.03% (w/v) of Tylose MH300 in water (usual ratio: 4 to 10 g per liter) and swell for 24 hrs at room temperature; homogenize the suspension in a high speed mixer, for 4 min at the temperature of running tap water; add any modifying materials, mix gently and leave the mixture for another 24 hrs; pour the suspension on a filtering device, recover the semi-dry sample and dry further between blotting paper and under weight.

Formaldehyde as a modifying agent was added as formol (37% formaldehyde in water). When formol was used, the first deposit was rinsed with distilled water until a negative reaction with fuchsin was obtained; then the rinsed deposit was resuspended in 0.03% Tylose, swollen and reformed by filtration. Any calcium carbonate added was analytical grade. Paper fibre suspensions were prepared from fragmented Tengujo.

Evaluation of reconstituted parchment

The tensile strength, the strength of the combination between old and reconstituted parchment and the slit tear resistance and thread tear resistance were measured on 2-cm wide strips, at a linear velocity of 15 mm/min, at 21°C and 55% relative humidity (Amsler type 0,2 ZH118 drawbench, A.J. Amsler, Schaffhausen, Switzerland). The thread tear resistance was especially introduced here and was measured by tearing the reconstituted parchment with a sewing thread after pricking. In order to be able to compare these mechanical parameters in a quantitative manner, it was preferred to express all as the force executed by a mass (in kg) needed to perform the action.

pH measurements were performed on aqueous extracts of parchment clippings (20 mg per ml), obtained after 24 hrs at room temperature in closed vessels under constant agitation.

The thickness of the reconstituted parchment was measured with a micrometer and a mean value was calculated from at least five measurements. By forming square sheets of 10 × 10 cm, using varying volumes of the same parchment pulp, a correlation could be established between the volume of parchment pulp and the thickness of a 100-cm² area of reconstituted parchment.

The structural compatibility of materials, including membranes of goldbeaters'

skin (GBS) eventually to be applied on top of contact zones, was checked by means of a scanning electron microscope (Jeol JSM6300, Jeol Ltd., Tokyo, Japan). The dimensional stability under ageing was measured on 100-cm² reconstituted parchment samples. Also, some other evaluation parameters were remeasured after ageing. The ageing conditions were the following: 30°C; 80000 lux on the sample surface (radiation filtered through a borosilicate filter); 35% RH for 3 hrs, gradient to 70% RH for 1 hr, 70% RH for 3 hrs, gradient to 35% RH for 1 hr; the 8-hrs cycle was repeated 30 times (Atlas XR35 Weatherometer, Atlas Electric Devices Co., Chicago, USA).

Preparation and properties of reconstituted parchment

The first attempts to prepare reconstituted parchment were made by grinding and suspending calf parchment. Several difficulties were encountered with this kind of material. When milled in its dry state, the tough parchment tended to burn, generating brownish reconstituted parchment sheets. Milling in water was often incomplete and tended to form gelatinous suspensions. Parchment dust, as recovered from parchment manufacture, gave brittle and weak sheets by the lack of appropriate fibrous structures in the dust.

Hide powder, prepared from limed, delimed, acetone dehydrated, and milled calf hides could be easily suspended in water. The reconstituted parchment was strong and homogeneous but highly transparent. After extensive experimentation, it was found that the transparency could be reduced by the addition of paper fibres or calcium carbonate, or by preliminary treatment of the pulp with formaldehyde. In Table II, some properties of reconstituted parchment prepared from hide powder and paper fibre or calcium carbonate are presented. The addition of paper fibre or calcium carbonate tended to decrease the tensile strength of the reconstituted parchment, but to increase its tear strength and thread tear strength. The effect of the added materials on the transparency is illustrated by the opacity.

Table II. Mechanical properties of reconstituted parchment, prepared with hide powder and paper fibre or calcium carbonate, or treated with formaldehyde; all amounts added are given as % (w/w); all strengths are expressed as the mass in kg, needed to perform the action; parchment pulp contained 2 g of hide powder in 200 ml of suspending liquid, except (*), which contained only 0.8 g of hide powder.

Additions	Tensile strength	Tear strength	Thread tear strength	Opacity %
None	33	0.15	0.9	22
5% Tengujo	30	0.35	1.1	43
10% Tengujo	16	0.30	2.0	54
20% CaCO ₃	25	0.30	2.1	61
Formol (*)	8	—	—	85

By forming sheets with different volumes of hide powder suspensions, a correlation could be established between volume of pulp and area and thickness of the reconstituted parchment obtained (See fig. 3).

Under the cited ageing conditions, the linear shrinkage of reconstituted parchment (sample prepared without any addition) was lower than 2%. The thinnest samples decreased about 10% in thickness (See table III).

In another set of experiments, the strength of the bond between genuine and reconstituted parchment was measured by leafcasting a sheet of parchment (10 × 10 cm) with a similar sheet of reconstituted parchment on the vacuum table, following the same practice as is used in practical leafcasting. Occasionally, the contact zones were covered with one layer of goldbeaters' skin, using 3% (w/v) Tylose MH300 in water (7). One set of samples was aged as described. All samples were cut in 2-cm wide strips and mechanically tested (See table 4). The strength of the parchment-reconstituted parchment bond was about one-tenth that of reconstituted parchment. For conservation purposes, the relative weakness of the bond may be considered as an advantage. The bond might be strengthened

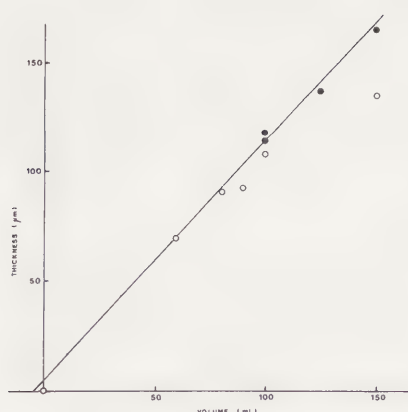


Figure 3. Correlation between thickness of reconstituted parchment formed and volume of parchment pulp used (containing 8 g of hide powder per liter) to produce an area of 100 cm² of solid sheet; o: 10% (w/v) of calcium carbonate added; o: pulp, pre-treated with formaldehyde.

Table III. Dimensional stability of reconstituted parchment; 8 g of hide powder per liter; no additions. NA = not aged; A = aged.

Volume (ml)	Dimension (mm)		Thickness (μm)	
	NA	A	NA	A
60	80	79	70	64
80	80	79	92	84
90	80	79	94	94
100	80	79	106	102
150	80	79	136	136

Table IV. Tensile strength of reconstituted parchment and of reconstituted parchment bonds; influence of goldbeaters' skin and ageing. NA = not aged; A = aged.

Sample	Break (kg)	
	NA	A
Pulp-parchment bond	3.0 ± 1.0	2.5 ± 1.4
Pulp alone	26 ± 3	26 ± 2
Pulp-parchment bond + GBS	4.3 ± 0.9	4.4 ± 0.6
Pulp alone	25 ± 5	25 ± 4

somewhat by the application of goldbeaters' skin. The ageing conditions used had only minor effects on the mechanical properties of these materials.

The pH measurements were performed on reconstituted parchment, prepared without any addition or with 20% (w/w) calcium carbonate or with formol (10 ml or 20 ml per 0.8 g of hide powder), before and after ageing (See table V). The pH of reconstituted parchment was only slightly influenced by formaldehyde derivatisation. Calcium carbonate increased the pH by 2 units. No pH value was changed considerably under the ageing treatment applied.

Table V. pH of reconstituted parchment preparations. NA = not aged; A = aged.

Reconstituted parchment composition (area = 100 cm ²)	pH	
	NA	A
0.8 g hide powder	5.60	5.64
2.0 g hide powder + 0.4 g CaCO ₃	7.66	7.75
0.8 g hide powder + 10 ml formol	5.42	5.56
0.8 g hide powder + 20 ml formol	5.22	5.22

The stability and compatibility of materials was investigated by leafcasting of a severely damaged sheet of old parchment with parchment pulp, prepared with formaldehyde, after preliminary relaxation of the old parchment at high relative humidity using the Gore-Tex membrane sandwich method (8). The following parameters were measured, before and after ageing: dimension of original parchment, dimension of the leafcast, solidity of the parchment-pulp bond, either covered with goldbeaters' skin or not, fibre structure of reconstituted parchment in cross sections of the contact zones (See table VI and figs. 4–5). The stability of both original parchment and reconstituted parchment was very high under the ageing conditions applied. The bonds covered with goldbeaters' skin were

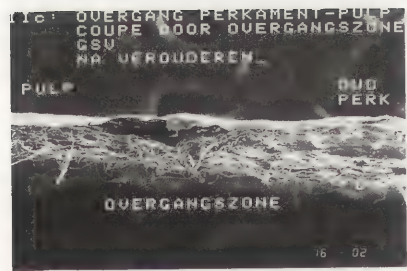


Figure 4. The combination of old parchment and reconstituted parchment, after ageing. The cross section shows reconstituted parchment (left), the contact zone (middle), and old parchment (right). The contact zone was covered with a sheet of goldbeaters' skin.

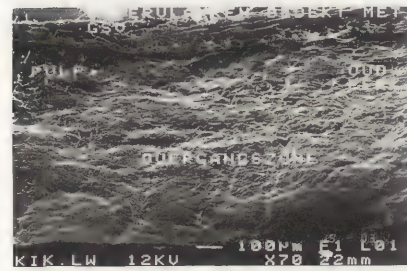


Figure 5. As figure 4 (surface view).

Table VI. Stability of a leafcast, performed with formol-treated parchment pulp. Ageing 1 = 25°C, RH change every hour between 30 and 80%, 18 days; ageing 2 = as ageing 1, 32 supplementary days; ageing 3 = 30°C, RH as ageing 1, 80000 lux on sample, 10 supplementary days.

Action	Dimension of old parchment	Dimension of leafcast	% of bonds broken	
			no GBS	GBS
None	190	—	—	—
Leafcast	191	—	0	0
Ageing 1	191	192	25	0
Ageing 2	191	193	31	0
Ageing 3	190	190	34	0

very stable, although some lifting of the membrane from the parchment surface could be observed after ageing (See fig. 4). About one third of the uncovered bonds were broken after all ageing periods. Since the majority of these broken bonds did already appear after the first short ageing period, these probably represent areas where the bonding was not effectively performed originally. The combination of the two materials may be followed as well in the cross section as in the surface structure (See figs. 4, 5).

Conclusion

The possible use of collagenous dermal tissue for the repair of severely degraded parchment was investigated. The transparency of samples prepared with pure hide powder may be reduced by the addition of paper fibres or calcium carbonate, or by preliminary reaction of collagen with formaldehyde. From measurements of acidity, mechanical, and optical properties, also after ageing, it followed that dermal tissue suspensions containing 10% (w/w) of Tengujo fibres or 20% (w/w) of calcium carbonate, or treated with formol (25 ml per gram of hide powder), may be used for parchment repair by leafcasting of relaxed parchment.

An asset of this kind of reconstituted parchment, when it is intended to be used for the repair of parchment that must be rebound, is its good resistance to break and tear (also by a sewing thread) and its rather weak bonding to the original parchment, eventually to be improved by the application of goldbeaters' skin. Further experimentation will involve some refinements on the sample compositions and preparation procedures and some additional ageing experiments.

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We thank Prof. Derolez (State University of Ghent), Dr. C. Coppens (Catholic University of Louvain), Prof. J.A. Szirmai (Oosterbeek, The Netherlands) and W. Smit (Royal Library, The Hague, The Netherlands) for fruitful discussions on problems and ethics involved with the rebinding of codices. We also would like to thank Dr. L. Wouters (K.I.K.) for her help with the SEM analyses.

Materials

Tylose MH300 (methyl hydroxyethyl cellulose). Hoechst, Frankfurt am Main, Germany.

Tengujo paper, 8.6 g/m². O. Vangerow, Ottobrunn, Germany.

Hide powder. Leather Trade House, Northampton, England.

Gore-Tex (PTFE membrane). Alois K. Diethelm AG, Lascaux Farbenfabrik, Brüttisellen, Switzerland.

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Working Group 15

Mural Paintings and Mosaics

Peintures murales et mosaïques



Abstract

This paper describes investigations carried out by the Danish National Museum in connection with the discovery of gothic wall paintings in a small Danish village church. Examinations of the painting technique, structure and composition of materials were carried out. The results indicate a rapid technique with use of little equipment and few materials. The degradation of red, blue and green colours is elucidated.

Keywords

Gothic wall paintings, painting technique, pigment degradation, copper pigments, minium, vermilion

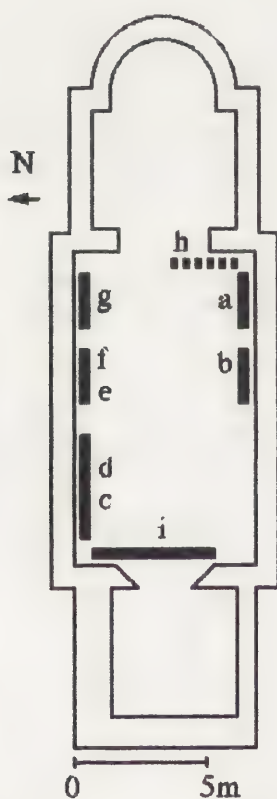


Figure 1. Plan of Gundsømagle church c. 1320 with the identified scenes a-i.

Early Gothic Wall Paintings: An Investigation of Painting Techniques and Materials of 13th-Century Mural Paintings in a Danish Village Church

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Introduction

More than 800 Danish churches have medieval mural paintings in varying states of preservation and every year new murals are discovered under the whitewash layers of the centuries. The gothic wall paintings described here are found in the nave of the Gundsømagle village church situated in north east Zealand. The church is from about 1100 and built of lime tufa (1). It was first decorated with romanesque paintings in the chancel and on the east wall in the nave (fig 1). In the thirteenth century the nave was altered. The early gothic paintings in the nave which are the topic of this paper were executed c. 1275. Around 1320 a brick tower was built with a decorated portal into the nave. Gothic style brick vaults and new windows were made at the beginning of the 16th century. This partly destroyed the wall paintings and the walls were whitewashed.

A fire in 1987 necessitated the uncovering of the wall paintings, which turned out to be the best preserved Danish early gothic paintings. The conservation project also involved a climate research program (2) and an archaeological excavation of the floor (1).

The subjects and layout of the early gothic wall paintings

The gothic wall paintings consist of an upper and a lower frieze with scenes from the childhood of Christ and scenes from the Passion. The friezes are framed by two ornamental borders and under the lower border a small curtain is painted. Altogether the decoration once covered an area of approximately 135 m². The scenes from the childhood are located on the south wall where two scenes can be identified as the Adoration of the Magi (fig 1-a) and the Massacre of the Innocents (fig 1-b and fig 2). On the north wall are scenes of the Entry into Jerusalem, the Entombment of Christ, Noli me tangere, the Incredulity of Thomas and the Ascension (fig 1-c-g). On the southern side of the east wall over the vault are fragments of what is probably the Birth of Christ (fig 1-h). On the west wall there is a Doomsday scene with Christ seated on a throne with four small souls in a cloth. Two angels with instruments of the Passion are standing at his side (fig 1-i and fig 3). In the lower parts of the west wall the paintings are partially destroyed by the portal, but the figure of Christ has not been affected. The scene is painted on a very uneven bumpy surface, a transition between a walled up window and the church wall.

The painting technique

In connection with enlargement of the romanesque windows in the nave, a layer of whitewash had been applied on all the walls including the east wall with its romanesque paintings. On the west wall parts, of the partially loose whitewash were removed just before the paintings were made, directly on this patchy ground.

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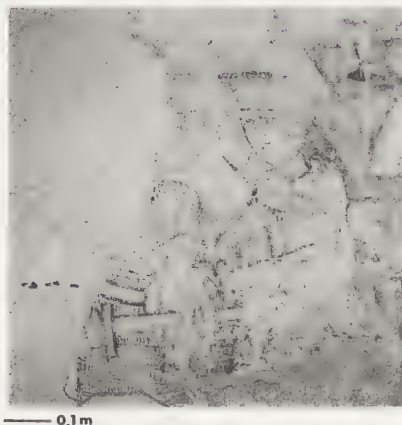


Figure 2. The Massacre of the Innocent. Scene from the south wall (fig 1-b).

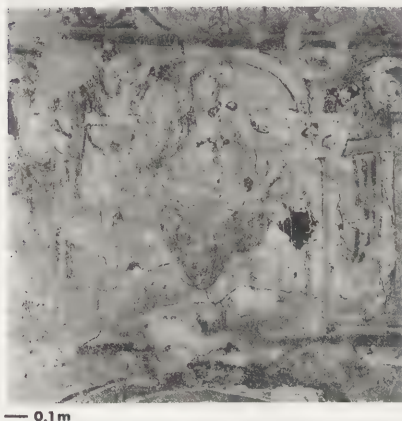


Figure 3. Domsday scene on the west wall (fig 1-i).

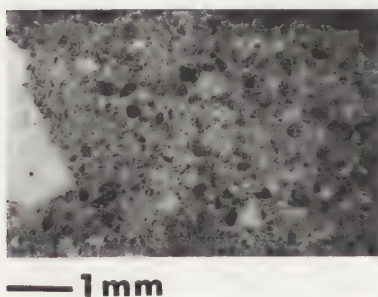


Figure 4. Cross section of plaster from the east wall of the nave. Dominating grain diameter of the sand c. 0.15 mm.

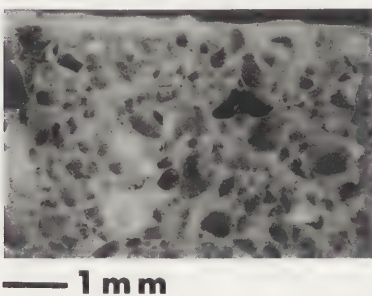


Figure 5. Cross section showing the plaster from the north wall. The sand has a dominating grain diameter of c. 0.35 mm.

The mural paintings were obviously executed very quickly without a previous marking out of the principal scenes by aid of rulers, compasses or plucked string. Only in one scene did we detect very thin scratches to mark the contour of a figure. This method is quite different from the laborious planning that is found in Romanesque painting (4). However, a detailed plan for the decoration must have existed. Circular elements in the painted haloes and architecture were executed by eye and the painter, for some reason, avoided precise vertical and horizontal lines as well as perfectly circular forms. In the different scenes the painter first roughly sketched the outlines of the figures, borders and architectural elements with a few thin painted lines. Next he laid the under painting. Then he painted the shadows in the figures and their robes and the background colours were applied. Finally the finer details, such as faces, were applied. The last stage in the painting was the outlines, painted in black.

The background was presumably covered with blue azurite which contrasted with the clothes and details painted with bright red vermillion, green copper pigments and orange minium. The different parts were only separated by narrow black outlines. The white colour of the plaster is the only white that is used. No high lights have been discovered. The flesh colour of the faces, hands and feet are not opaque, but formed with two different yellow shades and accentuation in red ochre. Inside the outlines of the more important sanctified persons' haloes, we found fragments of iron nails. This indicates that these figures had applied haloes probably made of gilded metal foil. These haloes were all the same size, 24 cm, and presumably mass produced. The only important figure without traces of an applied halo is Christ in the doomsday scene on the west wall.

We deduce that the painter worked from two portable scaffolds. The taller one reached the edge of the upper frieze 170 cm below the original flat ceiling. The other scaffold followed the lower frieze. The ornament border and the tapestry could easily be painted from the floor. This assumption is supported by the fact that there is no continuous horizontal line in the ornament borders but the lines are made by eye in the individual sections. On the west wall the scaffold has been fastened with a pole into the wall. The hole was later repaired with clay and pieces of brick. The painter then applied his colours directly on this surface. Scaffolding along all four walls at one time (a length of 37 m) would have been a considerable construction work and require a prohibitively large amount of timber.

The painting materials

There are two types of plaster on the walls of the nave in Gundsømagle Church. On the east wall we have a lime plaster in one layer (Fig 4) which is the same as the plaster under the romanese paintings in the nave. The plaster contain 16–18% calcium carbonate, 79–80% sand and 3–4% matter soluble in hydrochloric acid. The brown sand filler is of very small average particle size, 80% of it has a diameter between 0.3 and 0.1 mm. Such a composition is uncommon in Danish romanese mortars. A possible source of the sand has been located 1500 m from the church. The other walls in the nave also have a single layer of plaster (fig 5), but of a quite different composition. The mortar is richer in calcium carbonate, 20–22% and it contains 75–77% of a rather coarse sand filler (70% between 0.4 and 1 mm). Both types of plaster contain about 5–10% chalk grains (probably unburned lime). The cross sections, and examination of the walls with binoculars, show that there are normally two and sometimes three layers of white wash between plaster and paint layer. The romanese paintings on the east wall were also covered with whitewash before the early gothic paintings were made.

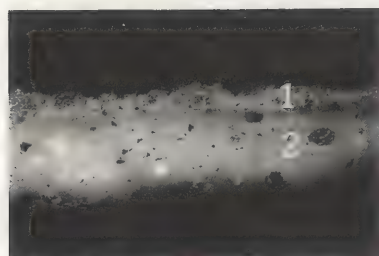
Relatively few pigments are found in the wall paintings (table I). This is quite normal for Danish gothic murals. Usually red and yellow ochres are the dominant pigments and red and yellow ochres rich in iron oxide are also found here.

There are only few areas of pure red colours in the paintings, all of them contain vermillion (fig 6). Other red and brownish colors contain vermillion plus a brown amorphous mass that contains manganese, lead and chlorine. Some dark brown

Table I. Selected pigments in the gothic wall paintings.

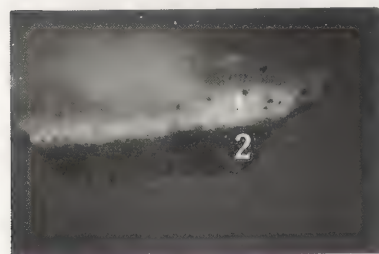
Colour/location	Analytical results	Comments
Blue on black ground, east wall over the vault	Azurite ^{abc} on charcoal ^a	Unchanged blue background colour
Green on black background, south wall	Basic copper chloride, Ca, (Pb) ^c charcoal ^a	Decomposed copper-blue mixed with lime on a background of charcoal
Green from cross, west wall	Basic copper chloride ^c atacamite ^d	Originally (?) green copper pigment without lime
Green from a repair, west wall	Basic copper chloride, Ca ^c	Copper pigment mixed with lime
Yellow, north wall	Iron oxide, silicates and CaCO ₃ ^{bc}	Ochre mixed with lime
Red, west wall over portal	Iron oxide, CaCO ₃ ^b and quartz ^a	Ochre mixed with lime (crushed brick?)
Black, north wall	lead dioxide ^{cc}	Decomposed minium
Brown, south wall	Mn, Ca, Hg, Pb, Cl ^c	Decomposed vermilion with minium, amorphous
Brown, south wall	Ca, Mn, Cl, Pb ^c	Decomposed vermilion with minium, amorphous
Red, east wall over the vault	Hg, S, Pb ^{cca}	Vermilion, minium(?)

Identification methods: ^a Optical microscopy; ^b Microchemical tests; ^c X-ray diffraction with Gandolfi camera; ^d FTIR- spectroscopy; ^e SEM/EDS.



— 0.1 mm

Figure 6. Cross section showing 1 vermilion on a layer of 2 white wash.



— 0.1 mm

Figure 7. Cross section from the background. 1 green copper chloride on a layer of 2 charcoal.

and black samples contain manganese, lead and chlorine but no mercury. One black sample consisted of pure lead dioxide.

The green colours consist of copper chlorides, in some samples identified as atacamite, one of 3 basic copper chlorides with the formula $\text{Cu}_2\text{Cl}(\text{OH})_3$ which are often found in copper corrosion products. Blue Azurite on a black background was found over the vault and in a tiny spot in a green area on the northern wall. Charcoal is found in the outlines and under the green copper chlorides (and azurite) in the background of the scenes (fig 7).

Many of the paint samples contain CaCO_3 . This partly derives from impregnation with limewater during the whitewashing of the walls. It is, however, obvious that lime has been mixed with some of the pigments as a binding medium. Very little calcium carbonate was found in most of the vermilion and lead containing pigments. This indicates that an organic binding medium was used for these colours. Analysis showed that some of the samples contain animal glue (5).

Colour change

The paintings as they are seen to day are obviously only fragments of the original decoration. Most of the loss is due to mechanical damage arising from renovation and maintenance of the building. But chemical changes due to adverse climatic conditions can also be observed. Green is a dominating colour today, and all examined greens consist of copper chlorides. Traces of blue azurite, and indications of different application techniques, makes us suggest that at least the green areas on the background were originally blue. This agrees with what is found in the Danish Romanesque wall paintings where the background is normally made with ultramarine on charcoal. The impact of chlorides, moisture and high pH during whitewashing over the centuries may have transformed copper pigments such as azurite and malachite into copper chlorides. Transformation of malachite is, however, not necessarily connected with perceptible colour change. The phenomenon has been observed elsewhere in Danish wall paintings from the gothic period and also in Austrian wall paintings (6) with azurite. In ancient Egyptian wall paintings even the relatively stable Egyptian

blue and green frit (calcium copper silicates) have been transformed into atacamite due to chlorides and moisture (7).

The black sample consisting of lead dioxide is almost certainly decomposed minium, Pb_3O_4 . The oxidation of minium to lead dioxide is very often observed in Danish mural paintings. The cause of this transformation is unknown but moisture, high pH and microbial activity seem to be a possible reason (8). There are only very small pure red areas left. These areas all contain vermilion and they seem to have been protected by mortar and plaster layers. Most red samples had darkened to a certain extent. In addition to vermilion they consist of a brown amorphous mass which contain manganese, lead and chlorine. In some of the dark brown samples no mercury was detected but only lead, manganese and chlorine. The amorphous brown substance was not characterized further but it is believed that we are dealing with a decomposed vermilion possibly mixed with minium. We suggest that vermilion was transformed into volatile elementary mercury and chlorine and manganese compounds might have migrated from the moist wall. Vermilion is often transformed into a black modification of mercury sulfide, possibly catalyzed by halides and moisture in the wall (9).

Experimental details

Cross sections were made from plaster samples taken from all the walls of the nave and from most of the paint samples. The samples were embedded in polyester and polished on SiC paper. The pigments were identified by the methods mentioned in table I. SEM/EDS was performed on the cross-sections, the other analyses were done on selected loose paint particles. The composition of the plaster was determined by the method and equipment of Jedrzejewska (10) with minor modifications. Sand was sieved through a set of sieves with apertures of 2.0, 1.0, 0.4, 0.2 and 0.1 mm.

Conclusion

The wall paintings were executed in a rapid technique. The painter painted directly on the existing partly damaged surface and did not improve the support with a new whitewash. He used lime only as a binding medium—primarily in the under paint and to whiten some of the darker tones. Some of the more intense final colours (vermilion, minium and azurite) must have been applied with an organic binding medium because as little as 2–5% calcium carbonate was found in these colours. The pigments containing the heavy metal ions of lead, mercury and copper have disintegrated and changed the colour balance in the paintings severely.

Acknowledgements

Tim Padfield is thanked for his helpful advice on the English manuscript.

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Abstract

In the spring of 1990, the Department of Antiquities of Israel carried out an *in situ* conservation intervention of a Roman fresco from a villa near Ein Yael, located in the vicinity of Jerusalem. The intervention was carried out according to the following principles: *in situ* consolidation of the fresco; use of products compatible with the original components; application of techniques similar to the ancient ones; use of local products and equipment, roofing and protection against water as preventive measures; and a maintenance program. In the spring of 1992, an examination of the structure confirmed the highly effective intervention.

Keywords

Mural painting, *in situ* consolidation, lime, lime mortar, hydraulic lime, Ein Yael, Israel

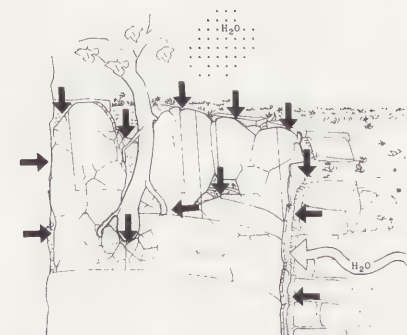


Figure 1. The fresco was still damp due to the migration of humidity from the back of the wall (white arrow). Significant deposits of dirt had penetrated between the various strata (black arrows). A large root grew in throughout the thickness of the fresco.

In Situ Consolidation of a Roman Fresco Near Ein Yael, Jerusalem

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Introduction

In the spring of 1990, the Department of Antiquities of Israel, with funds allocated by the Jerusalem Foundation, carried out a conservation intervention on a lining of one of the frescoes located in the thermal area of a Roman villa near Ein Yael, located in the vicinity of Jerusalem. The intervention, according to the agreement with the organizers, offered an opportunity for three local technicians to further deepen their professional experience by being part of the working team (1). The entire program was carried out according to the following principles: *in situ* consolidation of the fresco; use of products compatible with the original components; application of techniques similar to the ancient ones; use of local products and equipment, roofing, and protection against water and insolation; and a maintenance program.

By acknowledging these factors, we would like to stress the fact that an ancient structure must be respected not only for its aesthetic image but also for its components. The original techniques of construction must be recognized, and the structural and topographical context must be maintained.

The Roman villa situated in Ein Yael falls into the topology of rural residences used for the production of agricultural products, in this case, roses. Built at the end of the second century, it comprises two small thermal complexes, one of which is almost 4 meters in diameter with a multicolored mosaic floor geometrically arranged and bearing a large star in the middle. On the walls we find a layer of frescoes of imitation marble, which is conserved for nearly 3 meters and is almost 1.5 meters high in total.

In March of 1990, the area was excavated, revealing both the mosaic and the frescoes (2). The fresco was still damp, with a deposit of dirt covering the painted surface, large portions of fresco were detached and significant deposits of dirt had penetrated between the various strata, and a large root grew in the thickness of the fresco that was partially supported by the root itself (See fig. 1). The entire area was surmounted by an architectural structure in metal with a rainwater gathering system created for protection against insolation and rain.

The outer layer of the fresco is made of a scratch coat (*arriccio*) and *intonaco*: the first is applied directly on the wall, is dark and has a great percentage of large granulation; the second is composed of a white paste and has a homogeneous percentage of fine granulation. This technique dates back to the Romans who applied both scratch coat and *intonaco* in different layers to guarantee the carbonation of each individual layer.

Scratch coat (*arriccio*)

In the scratch coat one can distinguish two different layers of equal thickness, roughly 1 cm each and made of the same mixture; these layers were applied, however, in different stages. This solution was adopted in order to avoid an uneven carbonation due to the excessive width of the layers. The section clearly shows white lime putty granules not completely blended that stand out in the faint yellow tone of the paste, the color of which probably derived from the sand. One can also note some stringy traces which prove the addition of vegetable fibers; these fibers kept out the humidity. In this way, an excessively rapid disintegration of the mortar, detrimental to the final consistency, was avoided. This was a custom used both in the west and in the east, and its practicality was well known in early eras (3).

Intonaco and intonachino

The total thickness of the *intonaco* and the *intonachino* is generally less than 1 cm, but can even be double in thickness in relation to the point where the chiselling appears on the scratch coat. In the *intonaco*'s white mixture, which is not very porous, one can probably say that there is a greater percentage of lime than scratch coat.

The *intonachino* corresponding to the final setting to which the colors were added is not thicker than 3 mm, and was applied when the previous layer of *intonaco* had not been completely carbonated. This can be seen when looking at the perfect adhesion, at times indecipherable, of the two layers. The charge of the *intonachino* shows a compactness and a high mechanical resistance which has been augmented by the practice of dressing the surface before applying the colors. Glazing has been used to apply the colors, starting from the lightest background color to the final brushwork that imitates a darker veined marble. As for the pigments, natural earth has been adopted; for the color of the sole, a mixture of black and lime was used (4).



Figure 2. The state of conservation of the fresco: A) faults of cohesion of the *intonachino*, and B) faults of cohesion between the *intonaco* and the *intonachino*. Faults of adhesion between layers of mortar and the support of the wall include C) areas free of earth infiltrations, D) partial detachment of the *intonaco*, E) a total detachment from the *intonaco*, and F) areas found along the edges of the fresco.

Description of the condition of the fresco

The condition of the fresco is depicted in Figure 2. Investigation of the fresco's condition included examination of the faults of cohesion and adhesion.

The Type A deterioration demonstrated by the faults in the cohesion of the *intonachino* is due to the repeated cyclic phenomenon of the crystallization-solubilization of the soluble salts on the surface of the fresco. The salts found in the structure and in the ground are solubilized by the water, and move towards the surface where they crystallize once the water has evaporated. The therm-hygrometric changes, both in daytime and nighttime, determine a cycle of condensation-evaporation of the vapor followed by a salt movement and a deterioration of the superficial layer of the fresco.

The Type B faults of cohesion between the *intonaco* and the *intonachino* represented areas of limited extension. The detachment of these two layers is due to minute infiltrations of water which can only be seen in the cracked areas where the scratch coat has fallen off the wall.

The Type C faults of adhesion between layers of mortar and the support of the wall that are free of earth infiltrations show areas of limited extension, with an intermediate deterioration between the whole areas and those which are most detached. The different porosity between the stone of the wall and the mortar of the *intonaco* has determined a front of water evaporation which is higher in the inside than on the superficial plane of the fresco. This phenomenon, tied to the salt crystallization, is called subflorescence and has caused the detachment of the mortar layers of the support of the wall.

The Type D faults of adhesion between layers of mortar and the support of the wall with partial detachment of the *intonaco* are areas limited by broken edges and by areas concerned with a type C deterioration. Once the balance produced by the adhesion of the mortar to the wall is broken, the earth and minute root infiltrations have given birth to both lifting and bulging. These are areas of *intonaco*, at times very large, are completely covered in earth on the reverse side but still manage to maintain a partial contact with areas which have not been detached.

The Type E faults of adhesion between layers of mortar and the support of the wall presenting a total detachment from the *intonaco* are areas completely surrounded by broken edges. The natural growth of the roots and the increasing infiltrations of both water and earth have resulted in fractures of the *intonaco*, and often also overlapping of fragments which entirely compromised the adhesion to the support of the wall. These areas all show broken edges, a result of either the collapse of the wall, the destruction of the wall itself, or the penetration force of the same roots.

The Type F faults of adhesion between the layers of mortar and the support of the wall are areas found along the edges of the fresco. The collapse of the wall

structure has left, *in situ*, some fragments of intonaco void of their original support. These fragments were preserved like knife blades, and in certain cases they jutted out with respect to the trampling floor.

The intervention

The fresco was surveyed on a 1:1 scale by drawing with indelible markers on a sheet of polythene placed in contact with the surface. In this way, a precise documentation of the state of the fresco could be made, and used during the actual intervention.

Removal of the superficial deposits of earth was done with a dry brush and with the aid of a wet pad containing Neo-Desogen (5). The areas which were meant to be consolidated were initially cleaned with water. Infiltrations and alcohol were injected through existing minute cracks or by creating holes in the areas which showed color abrasions.

The consolidation was started from the deepest areas of adhesion faults to the more superficial ones, moving from the lower parts of the fresco towards the top, and from the areas which presented a minor degree of detachment towards those which were completely detached; in this way the most deteriorated areas were isolated by consolidated areas to which the next infiltration of consolidant could easily adhere. For this intervention, an hydraulic mixture of aerial lime made of lime putty and brick dust was used, a mixture capable of also adhering in the presence of the humidity present in the innermost layers of the *intonaco*. All the products used were found on site: the lime putty had been slaked for the past six months, and the brick dust was made on site by crashing the bricks and sifting the fragments of both ceramics and bricks.



Figure 3. *Velatura* of the type E and F deteriorated areas.

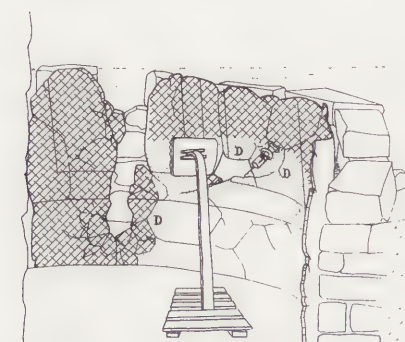


Figure 4. Consolidation of the type D deteriorated areas.

Removal of the earth from back of areas type D and E deteriorations and velatura of the areas presenting a type E and F deteriorations

As the consolidation progressed, it became possible to start removing the earth by using scalpels, spatulas, and micro-spatulas (metal wires flattened out at the extremities to fabricate long and flexible tools.) In certain points along the upper part of the fresco one noticed that the earth had penetrated for over 50 cm. Before removing, it was necessary to use *velatino* on the entire area and on the adjacent parts. Working with props which held the *intonaco* in place, it was possible to continue removing the earth until one encountered the wholesome areas or the areas already consolidated.

The structure of the permanently damp wall did not allow for adequate penetration and firm setting of the Acryloid B72 used to apply the *velatino*. By using acetone, it was possible to dehydrate the surface of the fresco. From the very beginning, a high concentration of Acryloid B72 was used in order to take the best advantage of its superficial setting (See fig. 3) (6).

Cutting of the roots and consolidation of the type D deteriorated areas

Cutting of the roots and consolidation of the areas presenting a type D deterioration is depicted in Figure 4. The roots deeply embedded in the wall were sawed off and a chemical herbicide (local production) for killing infested plants was applied. The consolidating intervention called for the restoration of the outer layer, the preliminary coating which was partly lost due to infiltrations from behind. Lime and brick dust was used where the brick dust was used as a charge to make an hydraulic mortar which would have been capable of somewhat isolating the humidity from the structure.

The only drawback to the use of lime mortar as a consolidant was, in this particular case, the waterproof barrier created by the *velatino* and the 20% Acryloid B72 which prevented a homogeneous front of evaporation for the exchange of humidity between the structure and its environment. This problem was solved by dampening and consolidating one area in half a day, in order to then have the time to take off the *velatino* before the lime mixture started its action of carbonation.



Figure 5. Consolidation was carried out in stages, starting with a liquid mixture, increasing the density and using some props.



Figure 6. Detachment and consolidation of type E deteriorated fragments. After applying the first liquid layer, the surface was ready to receive the new outer layer made of equal proportions of lime, sand, and brick dust.

In this way, it was also possible to disregard the irrelevant incompatibility of the Acryloid B72 with water; in the essential intervention of dampening the entire area to be consolidated, the quantity of water used was not limited, although it could have compromised the adhesion of the acrylic resin.

The consolidation was always carried out in different stages. Starting with a liquid mixture capable of filling the minute cracks, the density was increased according to the size of the detachments. To fill the back of all the upper edges of the fresco, after an initial infiltration of liquid mortar, a mixture of lime, local sand, and brick fragments was applied (7). This mixture was applied in different layers, depending on the depth to fill, and each layer was repeatedly shined on the surface with metal spatulas. Some props were placed behind the back of the areas which were filled (See fig. 5).

Detachment and consolidation of type E deteriorated fragments

For the area on the right of the root, once this had been uprooted, it was possible to take away the earth from all sides until the entire fragment was completely detached. A prop of the same size was used to secure the edges of the *velatino*; the fragments were removed from their support just enough to make it possible to clean the reverse.

The earth removal was done mechanically and with spouts of water which simultaneously prepared the surface for receiving the mixture of liquid lime and brick dust. After having applied this first liquid layer which acted as a final setting, the surface was ready to receive the actual new outer layer made of equal proportions of lime, sand, and brick dust (See fig. 6).

Consolidation of type A and B deterioration areas and final stuccoing

As the consolidation of the deeper layers was completed, work began on the more superficial detachments, still using the same mixture and the same technique of application. For the decorated parts where the surface of the *intonachino* was damaged, a liquid suspension of hydraulic lime was applied drop after drop with a syringe.

A mixture of lime and sand (1:2.5) was finally used to stucco the cracks and the holes on the plane of the fresco and to close all the edges of the breaks, thus covering up the layer of lime, sand, and brick fragment compound ("*cocciopisto*") and the infiltration mortar which was still visible.

Protection

When the consolidation of the fresco was concluded, its chance of survival obviously depends on the protective measures that are taken to prevent further deterioration. Water, as rain and as migrating water from the surrounding earth, is a primary concern; additional potentially damaging influences are the insulation and visitors.

As protection against rainwater and insulation, the extant metal roof was retained. This structure is strong enough to resist the wind, but not so "heavy" as to disturb the landscape of the site; it is open and high enough to avoid the risk of producing a "greenhouse effect," and has an efficient gathering system to collect rainwater away from the fresco.

The earth platform which rests on the back of the wall is an obvious vehicle of infiltration for humidity that could migrate from the surrounding earth. To limit this phenomenon, a draining ditch was built along the external perimeter of the wall. This ditch, deeper than the wall, takes in and disperses the humidity of the earth platform before it reaches the fresco, allowing the structure to dry off and to be ventilated on both sides (not simply on the surface of the fresco). The draining ditch as made it possible to restore the outside of the wall using a lime-based mortar and plaster. After the consolidation, the draining ditch filled up with gravel of various granularities. In this way, a double effect was obtained: the wall was consolidated and the circulation of water in the structure was limited.



Figure 7. The monument at the end of the intervention: a roof with a gathering system to protect the area from rain and insulation, a drainage ditch to protect from humidity migrating from the soil, and a balustrade to show visitors the view point.

At the same time, a structure was built that was capable of allowing easy access to the public, who could enjoy the monument without having excessive contact with the structure. Thus, the risk of damage was reduced by preventing the circulation of visitors in certain places (See fig. 7).

Conclusions

The intervention was carried out by five restorers in the span of three weeks. During this time, the consolidation of the fresco and of the wall was completed. This intervention did not remove the possibility of new problems of deterioration, but at least it created a stepping stone from which, with the aid of the protective measures adopted, one can assure to the entire structure—wall/fresco/mosaic—the stability of a balanced system comprising healthy and homogeneous structures.

But realistic and effective protective measures are represented by the simple and economic program of survey and maintenance that is guaranteed to the fresco in the future. Two working days every two years will be spent on protective measures. The field experience will tell us the feasibility of this estimation.

During the spring of 1992, a first survey was done. It was possible to ascertain the absence of humidity on the fresco: only a few localized deep consolidations and some bordering was required in places where the detachment was the result of the drying of the wall. Very few points required an application of a biocide for algae (8). A light cleaning was done in some areas which were whitish in color; this surface change was probably due to the migration of soluble salts when the outside surface of the wall dried slowly.

During this first survey, we had the impression that the monument was generally in good condition, particularly considering that the Israeli winter in 1992 was extremely cold and rainy. The time required for the first maintenance survey was, after two years, two working-days. We will continue monitoring this experience in the upcoming years, always keeping in mind that the direction of our working is: minimum intervention, good preventive practices, and regular maintenance.

Acknowledgements

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Notes

1. The restoration works were executed by Tedy Mazzola, Graleb Abu Diab, and Marc Goodman from the Israel Antiquities Authority, and by Roberto Nardi and Andreina Costanzi Cobau from Centro di Conservazione Archeologica, Rome.
2. Gershon Edelstein, "A Luxurious Roman Villa in Rural Jerusalem," *Biblical Archaeology Review* (1989): 1–11.
3. Vitruvius, "De Architectura," VII, chapter III.
4. L.P. Mora and P. Philippot, *La conservation des Peintures Murales*, Bologna (1977), 1–15.
5. NEO-DESOGEN, Ciba Geigy, a 10% solution. Used diluted in water at 0.2% (20 cc in 1 litre of water). It has the role of a surface active agent, thereby increasing the cleaning action of water.
6. *Velatino* was applied with Acryloid B72 diluted at 20% in trichloroethane, applied on a preparation coat at 15%.
7. *Coccipisto*: 1 part lime, and 2.5 parts of sand; roughly 20% brick fragments is added.
8. Lito 3. Ciba GEIGY.

Résumé

Essai de définir le degré de blancheur d'une nouvelle couche de badigeon. Description de l'esprit dans lequel on a badigeonné les églises et de l'interaction entre badigeon et objet d'art (meuble et immeuble). Mesurage de la couleur des plusieurs couches de badigeon ancienne.

Il n'a que peu de sens de tirer des conclusions purement rationnelles, vu le grand nombre des variables, parfois opposées (badigeons, objets d'art partenant aux badigeons, mécanismes de vieillissement). C'est pourtant important de détecter scientifiquement des "tendances" afin d'être capable de faire un choix esthétiquement cohérent, dans le double sens d'esthétique par intention et par estimation.

Mots clef

Badigeon, blanchiment, finition, peinture murale, mesurage de couleur, architecture, gothique

Le ciel est blanc . . . Réflexions à propos du reblanchiment du chœur et du transept de la Cathédrale Notre-Dame d'Anvers

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L'église blanche

L'évolution des arches de soutènement, arcs et chapiteaux, tribunes, triforium et voûtes . . . tout cela nous a été servi, à nous étudiants en histoire de l'art, tout au long des cours d'histoire de l'architecture. Néanmoins on n'a pas soufflé mot des couches de finition architecturale. Pourtant celles-ci sont très importantes pour la perception globale de l'intérieur de l'église.

Wilhelm Worringer invoque, parlant du gothique, un grand nombre d'arguments qui laissent supposer que les surfaces architecturales ont été pensées blanches. Ainsi, selon lui, l'architecture gothique n'atteint pas toute son expressivité grâce à, mais malgré la pierre (1). La pierre est dématérialisée dans l'intérêt d'une pure expression de l'esprit.(2) Ou encore: "... nous ne percevons pas l'aspect d'une cathédrale gothique comme le spectacle d'un processus de construction, mais comme l'éclat d'un désir transcendant exprimé dans la pierre" (3). Quand de surcroît il se plaint qu'à l'occasion de la restauration d'églises gothiques, on crée un gothique "sec, sans vie, froid" dans lequel on apprécie, mise à part une touche de romantisme d'ambiance, seulement l'aspect purement constructif pensé machinalement: ici on fait allusion à des couches de blanchiment (4). Pourtant le terme n'est pas mentionné et aucun autre mot ne fait allusion à une autre forme de finition de la surface architecturale. Worringer est loin d'être le seul à réagir de la sorte.

Cependant outre l'ensemble des observations matérielles convaincantes que l'examen du bâtiment permet de faire, il y a assez d'indications qui montrent qu'il est invraisemblable qu'un intérieur d'église en pierre nue soit "fini".

La "Madone dans l'église" de Jean Van Eyck (Berlin) présente certaines anomalies, par exemple dans l'éclairage et les proportions qui, si elles n'étaient pas volontaires, seraient incompréhensibles dans le chef d'un tel peintre. De là la dénomination de "Madone comme Eglise" ou "Madone dans le Ciel" donnée à cette peinture (5). L'idée de l'église comme représentation du Ciel ou de la Lumière Céleste ne constitue pas, de notre point de vue, un grand pas (6). Nombre de sources littéraires y font allusion (7). Doit-on, ou plutôt peut-on s'imaginer le Ciel comme un bâtiment construit en pierre même si ce bâtiment est insolite? Souvent on trouve, sur une couche de blanchiment et/ou de plâtre, un appareillage peint, et non seulement sur une maçonnerie en briques, mais aussi sur des murs en pierre de taille avec des joints fins et bien soignés. Les joints peints concordent rarement avec les joints réels. Les couleurs aussi, parfois même celles des pierres peintes, divergent considérablement de la réalité. A juste titre, puisqu'il s'agit de l'architecture du ciel, de la ville céleste de la Jérusalem éternelle, et non d'une architecture ordinaire, de tous les jours. Voilà pourquoi des murs qui n'en sont pas: représentés par une configuration qui imite un appareillage ou par une couche de blanchiment lumineuse qui semble rayonner et qui est en conséquence ressenti comme immatérielle (8).

A la Cathédrale d'Anvers on a joué encore d'une autre manière avec l'espace. Le diamètre des ornements peints sur les voûtes autour des clefs de voûte polychromes décroît régulièrement de la croisée du transept vers l'abside. En même temps la hauteur des voûtes vers l'abside augmente. La différence de hauteur est de 50 cm, la diminution du diamètre d'une voûte à l'autre est de 20 cm. De cette manière on a voulu faire quelque chose d'immense et d'insaisissable car l'ensemble ne répond pas aux règles de la perspective.

Dans les comptes des marguilliers de la Cathédrale d'Anvers on trouve continuellement mentionnées, entre 1430 et 1815, des dépenses pour la peinture, le

blanchiment, le noircissement et le grisaillement (9). Il s'agit ici de documents techniques proprement dits qui mentionnent éventuellement l'objet traité mais qui n'y attachent aucune méditation esthétique ou religieuse. Il faut attendre un texte daté de 1695 pour trouver mention d'une relation directe entre les moyens et le but. Un curé y compare son église au Ciel et ajoute que l'église ne peut représenter la Jérusalem éternelle que si elle est blanche, pure et claire (10). Sur les tableaux des peintres d'architecture hollandais on voit souvent des églises conformes à cette description. Il s'agit surtout de tableaux généralement postérieurs à 1650. Contrairement aux tableaux antérieurs, qui représentent surtout des constructions imaginaires, ceux-ci montrent habituellement des églises réelles où la présence de couches de finition lumineuses et blanches est souvent accentuée par la présence de fissures et lacunes (10). Trop souvent on considère que si ces églises sont blanches, c'est uniquement la conséquence de la Réforme. Il y a des raisons de croire que les choses ne sont pas aussi simples que cela:

A la Cathédrale d'Anvers, nous trouvons des peintures de voûtes des XVe et XVIe siècles posées sur une couche de blanchiment. Il y a d'ailleurs, comme rappelé ci-dessus, des documents qui parlent de blanchiment dès 1430. Les couches de blanchiment correspondant aux peintures de voûtes, se prolongaient au-delà des nervures. A certains endroits ces nervures continuent dans un mouvement ininterrompu jusqu'au sol. Autrement dit ces couches de blanchiment antérieures à la Réforme ont certainement recouvert toute la superficie architecturale. Un examen sur place n'a pas dévoilé beaucoup de peintures murales qui relèvent de la première couche de finition, de telle sorte qu'il faut conclure que dans une large mesure la première apparence de l'église était une image blanche.

A partir de la seconde moitié du XIIIe siècle une forte tendance à augmenter la lumière est perceptible (12). Grodecki parle même d'une "immense clarté de la nef" (par contraste avec les chapelles latérales plus obscures). Alors que dans une première phase les fenêtres n'étaient premièrement conçues pour éclairer, mais plutôt comme murs lumineux, créant une atmosphère mystérieuse en émettant une lumière rouge-pourpre, telles des pierres précieuses, dans une deuxième phase, la "caja cerada" fait place à un ensemble clair, frais et léger (13).

L'association de la beauté matérielle et de la béatitude spirituelle préconisée par l'abbé Suger, semble avoir fait place (sous la pression cistercienne, par crainte des forces cachées de l'art?) à une esthétique plus classique. La métaphysique de la lumière est prépondérante dans les deux cas mais dans la deuxième phase sa représentation plastique utilise des moyens moins suspects. L'atmosphère oppressante et païenne n'existe plus. En même temps la transition vers l'intérieur d'église propre à la Réforme n'est plus aussi grande qu'on ne le prétend d'habitude.

En définitive il nous semble matériellement impossible que toutes les églises aient été blanchies ou même stuquées de fond en comble au cours de la période relativement brève des troubles religieux (15).

Vu ce qui a été dit ci-dessus à propos de l'esthétique monumentale pendant la deuxième phase gothique et d'autre part vu la finition relativement colorée du XVIe siècle, on peut dans un certain sens considérer le blanchiment de la Réforme comme une réaction violente mais certainement pas isolée, à une tendance antérieure.

Quel blanc [recouvrait l'église]?

Nous nous sommes attardés ailleurs sur l'importance de la présence de plusieurs couches de blanchiment superposées pour la protection des monuments et des sites et surtout pour la restauration des peintures murales et de la polychromie architecturale (16). Par la même occasion on a aussi rappelé qu'au cours des siècles des oeuvres d'art ont été fabriquées dans l'intention de les placer dans la Cathédrale d'Anvers. Certaines s'y trouvent encore à l'heure actuelle. On a également souligné que l'intérieur de la Cathédrale a été régulièrement reblanchi. Il nous semblait donc intéressant, surtout parce qu'une nouvelle restauration était prévue, de définir le degré de blancheur des différentes couches de blan-

chiment et de déterminer la nuance à adopter pour la nouvelle couche, afin d'obtenir un effet fondé pour l'architecture comme pour les oeuvres d'art immeubles par destination. Ce n'est pas facile. Car s'il est possible d'identifier telle ou telle couche de blanchiment comme "contemporaine" de l'une ou l'autre oeuvre d'art dans la cathédrale, il est assurément impossible de pourvoir toute oeuvre conçue pour la cathédrale d'un fond de sa couleur originelle (compte tenu des phénomènes de vieillissement tant de l'oeuvre d'art que de la couche de blanchiment). Une pure moyenne arithmétique est loin de garantir un bon résultat. Pourtant il n'est pas inutile de déterminer des "tendances" et des "ordres de grandeur" selon des données objectives. Ce que l'on peut/doit en inférer est alors une question d'interprétation.

A l'aide d'un Colorimètre Dr Lange, on a déterminé la luminosité ainsi que la teneur en jaune par rapport au bleu et en rouge par rapport au vert (L^* , a^* , b^*). Ce système nous semblait le plus pragmatique. Ont été analysées: la plus ancienne couche de blanchiment du choeur, une succession de quelque 9 couches de blanchiment postérieures, la couche de blanchiment la plus récemment appliquée et enfin, dans le but de se faire une idée de la patine à venir, cette dernière couche recouverte de poussière provenant de dépôts de la nef. Enfin les parements en pierre de taille de la nef ont été sommairement examinés.

La couche de blanchiment originale présente d'assez grandes différences en couleur et luminosité. Ici et là on peut parler de taches. A une certaine distance, par un effet d'optique les taches se fondent en un beige moyen. On a mesuré une moyenne de:

L*=71,5 a*=2,6 b*=10,9

avec des pointes de:

L*=65,6-74,2 a*=1,8-3,5 b*=10,3-12,2

La luminosité moyenne correspond à une valeur Munsell de ca 8,6 (17). Le ton est jaune rougeâtre.

Les couches de blanchiment postérieures, à l'exception de la dernière (qui n'a pas été prise en compte parce qu'elle diffère trop des autres), ont donné une moyenne de:

$L^*=80,1$ $a^*=-3,9$ $b^*=9,2$

avec des pointes de:

$L^*=67,8-87,3$ $a^*=-2,6-4,9$ $b^*=6,2-12,7$

La luminosité moyenne atteint sur l'échelle de Munsell une valeur 9. Ensuite, les couches de blanchiment ultérieures sont sensiblement plus froides que l'originale.

La dernière couche de blanchiment (fin du XIX^e siècle?) se distingue surtout par sa valeur L* qui, avec 61,01, est plus foncée que l'original, plus foncée même que la moyenne des pierres de la nef, qui atteignent une valeur L* de 66,7.

Plusieurs raisons nous ont amenés à choisir de ne pas adopter d'office une couleur correspondant (directement) à la première couche de blanchiment du chœur, bien que des peintures aient été posées sur cette couche.

Comme a été déjà noté, la couche de blanchiment originelle est parsemée de taches grandes et petites, plus récentes. Créer une semblable impression moyenne alors que l'on applique une nouvelle couche signifierait qu'il faudrait soit la patiner, soit appliquer une couche uniforme relativement plus foncée. Cette dernière façon de faire aboutirait à une lourde vision de "crème au beurre" puisque la nuance ne naîtrait pas de la perception par l'oeil de ce mélange de teintes. Cette première façon de faire ne serait pas intéressante, ni du point de vue économique vu la grande surface, ni du point de vue technique vu le matériau. La couche de blanchiment invite plutôt à apporter une correction tendant à une plus grande clarté que l'inverse, à cause de la présence de matériaux organiques et, très probablement, d'incrustations calcaires, causes principales de son assombrissement.

Dans plusieurs cas on a constaté la présence d'incrustations calcaires clairement visibles à l'oeil nu sur la couche de blanchiment originelle, mais en-dessous des couches postérieures. Ces dépôts étaient plus foncés et plus chauds en couleur que la couche de blanchiment originale (18).

En ce qui concerne la présence de produits organiques, on peut affirmer que nos laboratoires ont découvert dans la dite couche une quantité de 6,78% en poids de matière organique. Un examen plus approfondi doit préciser de quelles matières il s'agit.

Seule la première couche de blanchiment est notablement plus chaude que les autres. La première et la dernière sont aussi plus foncées. Puisque les couches successives font aussi partie de la "vie" de la cathédrale et qu'elles ont formé le décor original de nombre d'oeuvres d'art (par exemple la "Descente de Croix" de Rubens), il faut également en tenir compte dans la coloration de la nouvelle couche.

Par patinage naturel l'harmonie des couleurs se modifiera. Il faudrait anticiper cette évolution. On sait que les couleurs claires bleuissent sur un fond foncé tandis qu'inversément les couleurs foncées, sur un fond clair, tendent vers le rouge (19). Suggérer le bleu en voilant du noir avec du blanc est un vieux truc basé sur cette technique. Par conséquence des dépôts de poussière n'assombriront pas seulement les couches de blanchiment, elles les réchaufferont aussi. Un dépôt de poussière d'environ 10 ans d'âge a été récupéré de la nef et saupoudré sur un échantillon de la nouvelle couche de blanchiment. La couleur de cette nouvelle couche de blanchiment a été déterminée selon une méthode empirique, parce que nous ne possédions pas encore d'appareil de mesure. Nous avons mesuré les valeurs suivantes avec le Colorimètre:

nouvelle couche de blanchiment:	L*=88,7	a*=0,95	b*=7,3
idem avec poussière:	L*=82,0	a*=1,5	b*=8,2

Les mesures confirment la tendance supposée étant donné qu'ignorant la quantité et le type des poussières, ainsi que la manière dont le dépôt se formera, il nous est difficile de faire des prévisions exactes et encore plus d'effectuer une simulation.

Conclusion

La couche de blanchiment actuelle, qui apparaît un peu trop claire et trop neuve pour le moment—mais un jour elle sera trop foncée et trop sale—s'accordera à la valeur lumineuse des couches de blanchiment antérieures. La couleur sera quelque peu plus rouge que la dernière, mais plus froide que l'originale (en son aspect actuel). Elle sera un peu moins jaune que l'originale et que la postérieure. Dans l'ensemble nous estimons que la couleur convient assez bien au but de la Cathédrale: une Jérusalem Céleste blanche, propre et claire.

Les murs déplâtrés de la nef centrale sortent de ce cadre non seulement par leurs structure et texture, mais aussi parce qu'ils sont assez foncés:

L*=66,7	a*=1,7	b*=9,9
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avec des pointes de:

L*=57,8-72,4	a*=-0,1-7,1	b*=3,5-15,5
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Lors de la restauration d'églises on emploie souvent les termes "réserve" et "très neutre". Nous pensons qu'il faut être plus audacieux vu les intentions qui ont présidé à la construction des églises et à condition que l'un et l'autre soit le moins destructif et le plus réversible possible.

Pour finir nous voulons encore rappeler un passage de Wolfgang Schöne, où il parle de l'effet des murs blancs sur des peintures (20). D'un côté l'éclat des couleurs serait trop accentuée, de l'autre côté la lumière peinte en fonction de l'éclairage de ce qui est présenté serait dévalorisée. Pour ces raisons, il déconseille l'utilisation de murs blancs dans les galeries et les musées. Dans la Cathédrale, nous avons cependant affaire à une donnée historique. Peut-être peut-on justement trouver là une explication (complémentaire) des nombreuses "ombres"

noires ou grises peintes autour de tableaux ou de sculptures. D'un autre côté le cadre blanc accentue le caractère plastico-explicatif de la lumière peinte aux dépens du caractère réaliste-révélant.

En tout cas, voici peut-être la conclusion proprement dite, pour la restauration d'une église: un concept global, envisageant la mise en valeur de tout l'ensemble est indispensable. Dans ce concept la finition des murs joue un rôle du premier plan.

(traduction: J. Rachel et J. Deberg)

Notes

1. W. Worringer, *Vormproblem der Gotik*, (Antwerpen, s.d.), p.97.
2. *ibid.*, p.98.
3. *ibid.*, p.100-101.
4. *ibid.* p.102.
5. H. Sedlmayr, *Die Entstehung der Kathedrale*, (Zürich, 1950), p.491-492.
6. *ibid.*, p.95.
Worringer, "Vormproblem", p.70, 75.
7. Sedlmayr, "Die Entstehung", p.96-117.
8. O. von Simson, *The Gothic Cathedral. Origins of gothic architecture and the medieval concept of order*, (New York, 1956), p.7.
9. L. Van Langendonck, *Onze-Lieve-Vrouwekathedraal te Antwerpen. Historisch onderzoek van muur- en gewelfschilderingen in koor en kruisbeuk*, (Antwerpen, 1988), p.8.
10. G.E., "Over het witten der Antwerpse hoofdkerk", *De Vlaamsche school*, (1875), p.104-105.
11. Cath. expos., Rotterdam, *Perspectieven: Saenredam en de architectuurschilders van de 17e eeuw*, (Rotterdam, 1992).
12. L. Grodecki, "Le vitrail et l'architecture au XIIème et au XIIIème siècles", *Gazette des Beaux-Arts*, VIème période, tome 36, (Paris, 1949), p.20.
W. Schöne, *Ueber das Licht in der Malerei*, (Berlin, 1977, 4ème ed.), p.41.
Y. Vanden Bemden, "Geschiedenis van de Glasschilderkunst in Vlaanderen", *Glas in Lood (M&L-cahier 1)*, (Brussel, 1992), p.15-16.
13. Grodecki, "Le vitrail", p.22.
Sedlmayr, "Die Entstehung", p.396.
V. Nieto Alcaide, *La luz, simbolo y sistema visual*, (Madrid, 1989), p.62.
14. E. Panofsky, *Meaning in the visual arts*, (Harmondsworth, 1970), 1ère ed. 1955), p.167.
15. Van Langendonck, "Onze-Lieve-Vrouwekathedraal", p.11.
16. W. Schudel, "Couches de finition architecturale dans la Cathédrale d'Anvers", 5ème conférence à l'occasion des Journées d'étude de la SFIIC "Les anciennes restaurations en peinture murale", (Dijon, 25-27 mars 1993).
17. G. Thomson, *The museum environment*, (London, 1986, 1ère ed. 1978), p.60.
18. Nous avons trouvé ce type d'alteration sous cette forme par exemple à St. Agatha-Rode dans l'église Ste. Agathe et à Gand dans l'ancien Couvent des Dominicains.
19. H.D. Murray, *Colour in theory and practice*, (London, 1952), p.10-11.
E. Berger, *Katechismus der Farbenlehre*, (Leipzig, 1898), p.130.
20. Schöne, "Ueber das Licht", p.263.

Abstract

The painting technique was studied on the altar bar of the Assumption Cathedral forming a single ensemble with the Cathedral's iconostasis. Artists under the direction of Dionisius are believed to have painted the altar bar immediately after construction of the Cathedral was completed in the late 15th century. Spectral and X-ray diffraction (XRD) analyses of paint pigments were carried out. Paint components included azurite, ochre, glauconite and cinnabar. The paint composition on the faces and hands of the personages and the technique of face painting were identified. The composition of the "sankir" (the preparative layer) below the paint used on the faces was analyzed. The study included an examination of certain variations in the colour and composition of "sankirs" of images from different areas of the altar bar.

Keywords

Mural painting, 15th century, painting technique, paint pigments, spectral emission analysis, XRD analysis

A Study of the Technique of the Altar Bar Painting in the Assumption Cathedral of the Moscow Kremlin

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Introduction

The altar bar occupies the central place in the pictorial decoration of the Assumption Cathedral. Twenty half-figures of saints, monks and hermits have survived on the altar bar painting. Scholars believe the altar was painted in the late 15th century, i.e. immediately after construction of the Cathedral was completed. The altar bar painting is ascribed to the first murals of the Assumption Cathedral, along with the frescoes of the Pokhval and Peter and Paul side Chapels and the altar [1,2].

The first publications dealing with the altar bar painting appeared in the late 19th century when the iconostasis and the oak panelling covering the painting were removed during repairs [1-3].

Opinions are divided as to the date of the painting. The majority of scholars attribute the altar bar painting to the first iconostasis in the Assumption Cathedral, created by artists under the direction of Dionisius according to chronicles of that time.

Many scholars note a certain artistic affinity between the altar painting and the subsequent works of Dionisius and the artists of his circle [4,5,6]. This prompted a particular interest in the technique of this painting.

With regard to the number of artists who originally worked on the altar bar painting, all the scholars believe that at least three or four artists took part. Many scholars have recognized the high quality of the images on the northern part of the bar and ascribe this work to the most talented artist. According to scholars, two or three other artists worked on the middle and southern parts.

The altar bar painting was subjected to a close examination at the end of the last century, yet no data on technique or the paint composition were published.

The altar bar painting has undergone few changes in comparison with other murals of the Cathedral since the mid-16th century. It was subjected to less refreshing and renovating because it had been covered first by a range of icons, and then by an oak panel. In the late 1970s, when the panelling was removed, the painting reacquired its original appearance and became accessible to scholars. The painting was studied in the following ways:

1. The painting was examined visually in ordinary and oblique light using both magnifying glass and microscope.
2. After thorough analysis of the results of these observations, photographs were taken.
3. Microsamples from the paintings were taken, and a detailed study of the paint composition was carried out under laboratory conditions using microchemical, powder XRD, spectral and petrographic analyses. The results of the XRD analysis for the blue, green and red paint pigments are listed in Table I.

The green pigment sample was taken from the lower part of the painting, the blue pigment was taken from the background, and the red pigment was taken from the dividing belt. The analysis was carried out on the DRON-1 installation with the following operating conditions: U=35 kV, I=12 mA, source of X-ray radiation Cu-anode.

From the analysis the following facts were established. The main "d" lines for the blue paint spectrum belong to azurite and calcite. This identification had a good agreement between experimental "d" values and those for azurite and

Table I. Results of XRD analysis of minerals of paints from the altar bar of the Assumption Cathedral.*

Blue background		Azurite ASTM 11-682		Calcite ASTM 24-27		Malachite ASTM		Green paint, the lower part of the bar		Glauconite ASTM 9-439		Calcite ASTM 24-27		Red dividing belt		Cinnabar ASTM 6-0261		Calcite ASTM 24-27	
d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I
12,92	2							10,16	3	10,1	10			4,02	2			3,85	2
7,49	3							8,84	2					3,40	4	3,38	10		
5,47	7							8,40	1					3,25	1	2,92	3		
5,34	6	5,2	10			5,06	8	7,69	1					3,10	10				
4,87	2	5,15	6					6,70	2					3,03	5			3,03	10
3,80	6							5,91	1					2,94	5				
3,65	10	3,67	5			3,69	*	5,52	1					2,56	2			2,49	1
		3,52	10					4,49	2	4,98	*			2,30	4			2,28	2
3,47	2							4,54	2	4,52	8			2,10	3	2,07	6	2,09	3
3,12	4	3,10	2	3,03	10			4,43	2	4,35	2			2,02	2				
3,01	2							4,22	2	4,12	1			1,98	3	1,94	1		
2,89	2					2,80	*	4,02	2					1,90	2			1,91	2
2,67	2							4,00	2										
2,57	6	2,59	2					3,86	3			3,85	2	1,87	2			1,87	1
		2,54	2					3,64	2	3,63	4			1,76	2	1,76	5		
		2,52	2					3,03	10	3,33	6	3,03	10	1,70	1				
		2,51	3					2,88	1	2,89	5			1,62	2	1,46	3	1,51	1
2,31	4	2,33	2					2,69	2	2,67	1								
2,23	4	2,29	1					2,63	1										
		2,28	4					2,59	1	2,58	10								
		2,26	3					2,50	3			2,49	1						
2,14	2	2,22	7	2,09	3			2,29	4	2,26	2	2,28	2						
1,99	3	2,17		1,91	2			2,26	1										
1,85	3	1,93	2	1,87	4			2,17	1	2,15	2								
1,61	3	1,59	2	1,60	2			2,10	3										
1,53	3	1,51	2					2,09	1			2,09	3						
								1,95	1			1,91	2						
								1,91	3			1,87	1						
								1,66	1	1,66	3								
								1,51	2	1,51	6	1,51	1						

* The analysis was carried out on the DRON-1a installation, working conditions: U = 35 kV, I = 12 mA, source Cu-anode 1.5418 Å.

calcite, as listed in the ASTM card index (NN 11-682 and 24-27 respectively). The elemental composition of the blue pigment is listed in Table II, where it appears that copper is the most common element. Silicon, aluminum and calcium were also present in the dirt and whitewash.

The XRD analysis of the green paint allowed us to identify glauconite from the paint's components, with a good agreement between the "d" values and

Table II. The elemental composition of paints on the altar bar of the Assumption Cathedral.*

Sample	Elements								
	Si	Al	Fe	Ti	Mn	Ca	Mg	Cu	Hg
Blue background	h	h	p	tr	—	vh	p	vh	—
Red belt	vh	h	h	p	—	vh	p	tr	h
Green paint, the lower part of the bar	vh	vh	h	p	—	vh	h	p	—
The brown mantle of Theodosius the Great	vh	h	h	p	p	vh	h	p	p

Abbreviations: traces—tr, present—p, high content—h, very high content—vh.
* The laser induced emission spectral analysis was carried out on the LMA-1a installation (Karl Zeiss).

literature values for glauconite (ASTM N 9-439). The spectral analysis data confirmed that glauconite was the green pigment in the paint. According to our analysis, the pigment contained silicon, aluminum, iron, magnesium and calcium (Table II); the first four elements are in agreement with the composition of glauconite, while the presence of calcium confirms the presence of whitewash in the paint.

We interpreted the results of the XRD analysis of the red paint in favour of cinnabar because "d" values (Table II) were obtained which showed good agreement with the literature values for cinnabar (ASTM N 6-0261).

An examination of the paint samples under a microscope showed that the pigments used by the artists for making these paints were natural minerals. Azurite was represented by large blue particles, occasionally with green malachite crystals and particles of dirt. Glauconite consisted of large dark-green particles, while cinnabar was a mineral of perfect quality containing large and medium-sized bright-crimson particles. All the paints contain whitewash, composed of small-grained homogenous particles of calcium carbonate.

Thus, it was established that the blue background on the altar bar had been painted with azurite on top of a layer of black charcoal pigment. The azurite has been partially (and occasionally even totally) lost from the surface, and a black coal preparation can be seen practically everywhere through the layer of blue paint. The preparative layer is dense and even, and contains particles of coal and calcite. Cinnabar is the pigment in the red paint of the dividing belt, and pure cinnabar can also be found in the binding of Goshel in the hands of John-of-the-Tent. In all of the other paint samples, cinnabar is present in combination with other pigments. This conveys to the paints a number of tints, ranging from warm flesh-colour and rose to deep brown. Yellow paint on the faces, nimbi and garments of the Prophets contain a goldish, very fine-ground ochre found as a rule mixed with whitewash. The white paint on the scrolls, beards and hair are typically a lime whitewash. Ground coal is representative of the black paints.

As the analysis has shown, the painting technique on the altar bar was fairly complex. Areas of light and shade in the faces and garments of the personages were painted using a multi-layer technique. In the present paper special attention was paid to the study of the artist's technique of painting the exposed areas of flesh, hands and faces of the saints. The smooth transition from the darker layers of the ground to the upper lighter layers is a trait characteristic of Russian mural paintings of the 15th century. The painting of the altar bar is a typical example of modelling the volume of an image in this way. It is worth noting that in the shaded areas, the preparative layer remains exposed and was not covered by the upper layers of paint. This permitted study of the preparative layers. It appears that the ground differed according to colour and the composition of pigments in different areas of the bar.

In Table III, the composition of samples of ground from four groupings of images of saints on the bar is given. For the first group, a yellow-green colour of the "sankir" is typical. The "sankir" contains ochre, coal, glauconite, red ferric oxide pigment, cinnabar and whitewash. The ground of the face of the youngest personage, John-of-the-Tent contains the highest ratio of red pigments. The image of the first personage on the left side of the altar, Alexis the God's man, stands out from this group because of the richness of tint, and complexity of modelling of the folds in his dress. The colour of the ground in the second grouping of saints is yellowish, and in the third group, snuff-colour.

The ground of the second grouping of saints contains mostly ochre, a few coal and red pigments, azurite and whitewash. The ground of the third group contained ochre, a small quantity of glauconite, red ferric oxide pigment and a trace quantity of coal.

We ascribed the personage depicted in the southern part of the bar to the right of the royal gate (e.g. the Prince Ioasath) to the fourth grouping of saints. The ground of the face of this personage is the thickest, several times thicker than

Table III. The composition* of "sankirs" in the paints of faces of saints on the altar bar of the Assumption Cathedral of the Moscow Kremlin.

Group of personages	Yel-low ochre	Glauconite	Coal	Cinnabar	Red ochre	Azurite	White-wash
Group I							
Alexsis, God's man	vh	+	+	+	+	—	vh
Parthenius Lampsacenus	vh	++	+	+	+	—	vh
John Climacus	vh	++	+	+	++	—	vh
John-of-the-Tent	vh	++	++	+	+++	—	vh
Group II							
Paul of Thebes	vh	—	+	—	+	+	vh
Moises Murin	vh	+	+	—	+	—	vh
Theodosius the Great	vh	tr	+	—	+	—	vh
Group III							
Isaac the Syrian	vh	+	tr	—	—	—	vh
Ephraim the Syrian	vh	+	+	tr	tr	—	vh
Group IV							
The Prince Ioasath	vh	+++	++	—	++	—	vh

* Codes: tr = traces; + = low content; ++ = present; +++ = high content; vh = very high content.

is seen for the other groupings. This thicker ground is a greenish colour, and contains ochre, large particles of glauconite, red ferric oxide pigment and white-wash (Table III).

Thus, according to the composition and colour of the "sankirs", we divided the examined images of saints into the four groupings described above. This division coincides with the differences in the painting technique as revealed by stylistic analysis and a study of the iconography of the personages.

However, besides these differences, traits common to the painting of the altar bar must be stressed. These are: the same set of pigments for paint preparation, a similar manner of modelling the volumes of figures and faces, and the technique of painting the faces. The painting of the faces in all the images is executed finely, showing a gradual transition from the dark "sankir" to the lighter outer layers of paint. The ground was left exposed in shaded areas. This technique of mural painting is very similar to that used in painting icons.

Conclusion

A detailed analysis of the composition of paints and the technique of paintings on the altar bar of the Great Assumption Cathedral in Moscow was carried out. It is attested that the paint pigments are natural minerals, i.e. azurite, ochre, glauconite and cinnabar. The technique of painting on the altar bar proved to be fairly complex, multilayer and very similar to that of icon painting. It was found that for the volume modelling of faces and hands, the artists of the 15th century executed their painting upon a coloured "sankir". The composition of "sankirs" from different areas of the bar was determined.

Note

"Sankir" is the Russian name of the first special preparative layer under the paint layers of flesh-tone parts of human bodies (for example, faces, hands).

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Working Group 16

Resins: Characterization and Evaluation

Résines: caractérisation et évaluation



Abstract

New fluorinated polymeric materials with variable fluorine content and distribution were prepared by free radical polymerization of acrylic or methacrylic esters of different fluorinated alcohols such as trifluoromethylethanol, pentafluoropropanol and perfluorodecanol [$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{OH}$]. Different copolymers of the above monomers with nonfluorinated comonomers were also prepared. These materials were subjected to preliminary tests for photooxidative stability and stone protection efficiency. Fourier-transform infrared analysis show that the fluorinated systems display, in general, only moderately better stability with respect to nonfluorinated analogs. Stone protection behaviour seems to be very dependent on fluorine content but also on the nature of the lithotype. In particular, polypentafluoropropylmethacrylate (PPFPM) maintains a very good hydrorepellency after many hours. Other parameters (contact angle and color index) show less clear trends, indicating the need for additional research.

Keywords

Fluorinated polymethacrylate homopolymers/copolymers, photooxidative stability, stone protection

A New Class of Fluorinated Acrylic Polymers: Protective Materials for Stone

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Introduction

In a previous paper different approaches for the preparation of partially fluorinated polyacrylates were discussed (1). Synthesis of methacrylates of commercially available partially fluorinated alcohols appeared to be the easiest way to obtain the desired monomers (2). Thus, 2,2,2-trifluoroethylmethacrylate (TFEM) and 2,2,3,3,3-pentafluoropropylmethacrylate (PFPM) were prepared and converted into the corresponding polymers by free radical polymerization. The photochemical stability of PPFPM and its efficiency in the protection of different lithotypes was preliminarily checked by determining water absorption, contact angle, permeability and hydrorepellency (3).

In the present paper a more detailed study dealing with the preparation of homo- and copolymers of several fluorinated acrylic monomers such as TFEM, pentafluoropropylmethacrylate (PFPM), perfluorodecylacrylate (XFDA) and perfluorodecylmethacrylate (XFDM) is reported with the aim to prepare polymeric materials with variable amounts of fluorine atoms replacing H-atoms in the side chains (4, 5).

The chemical and photochemical stability of the above polymers was evaluated by IR analysis after UV irradiation in a climatic chamber under fixed thermohygrometric parameters to simulate outdoor conditions. The different tests carried out on the stone samples allow for the evaluation of the protective properties of the newly-synthesized polymers especially if compared to Paraloid B72 which is generally used in the restoration of monuments.

The results are discussed in an attempt to relate fluorine content and substitution of H with F in specific positions of the polymer structural unit to the stone protective behaviour.

Experimental protocol

The experimental protocol involved preparation of monomers, polymerization experiments, and the determination of the stability and protective properties of fluorinated polymers.

Preparation of monomers

TFEM, PFPM and XFDM were prepared by the following experimental procedure. The fluorinated alcohol (2,2,2-trifluoroethanol, 2,2,3,3,3-pentafluoropropanol or 1H,1H,2H,2H-perfluorodecanol, 0.1 mole), triethylamine (0.2 moles), 2,6-ditertbutyl-4-methylphenol as polymerization inhibitor (trace) and ethyl ether as solvent were introduced in a 250 ml flask and methacryloyl chloride (0.13 moles) was dropwise added at 0°C with stirring. During the reaction, a white solid product was formed. The reaction was carried out by stirring at room temperature for 24 hours. The ether solution of the acrylic

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ester was washed with water and then subjected to fractional distillation. The products were obtained as colourless liquids.

TFEM, 80% yield, b.p. = 30°C at 40 mmHg

PFPM, 70% yield, b.p. = 90°C at 760 mmHg

XFDM, 80% yield, b.p. = 70°C at 0.2 mmHg, purification by LSC (silica gel, chloroform/n-esane 5/1 as eluent).

XFDA was prepared by a similar route in 70% yield, starting with acryloylchloride.

Polymerization experiments

Polymerization experiments were carried out under nitrogen in a glass reactor under magnetic stirring and external heating by a thermostatic bath. The homopolymerizations and copolymerizations (see tables I and II) were performed in organic solvent solutions (CH_3CN , dioxane, or THF) in bulk using *a,a'*-azobisisobutyronitrile (AIBN) as free radical initiator.

Polymerizations were stopped by pouring the reaction mixture in various organic solvents: methanol, n-hexane, n-pentane or 1,1,1-trichloro-2,2,2-trifluoroethane (trade name delifrene, CCl_3CF_3). The polymer, separated by filtration, was dried under vacuum at room temperature.

Average molecular weight and molecular weight distribution were evaluated by GPC analysis (Perkin Elmer mod. LC-25, solvent THF or CHCl_3). Molecular structure of the polymers was checked by Fourier-transform infrared analysis (FTIR) and nuclear magnetic resonance analysis (CDCl_3).

Stability and protective properties of fluorinated polymers

The photostability of these polymers as compared to commercial nonfluorinated polyacrylates and polymethacrylates (Paraloid) was tested.

Before weathering, all the samples were examined by IR techniques. The artificial weathering was carried out by exposing the polymers to UV irradiation for 72 hours using a HPK 125 W Philips mercury lamp with emission peaks in the range 580–250 nm in a climatic chamber maintained at 25°C and 10% relative humidity. All the polymers were placed on a slowly rotating plate 30 cm from the lamp for uniform exposure to UV irradiation.

To check the efficiency of the new polymers as protective agents, a set of tests was carried out on a representative polymer. For this purpose, 5 g of poly(pentafluoropropyl methacrylate) (PPFPM) (10% solution in CHCl_3) were applied by brush on the stone samples.

Three different lithotypes were used for their wide presence in historical monuments and for their different origin and porosity:

- Carrara marble = low porosity (1%) rock, composed of calcite
- Vicenza stone = medium porosity (12–15%); biosparite with an abundant skeletal material in the fine carbonatic matrix
- Verona red = very low porosity (0.2–0.4%); organogenic limestone formed by compact calcareous nodules, surrounded by marly material.

The following tests were performed according to the Normal Recommendations, before and after the treatment with the chosen protective agent, of water absorption by capillarity, water absorption at low pressure, contact angle (measured with a Surface Wetting Tester Lorentzen Wettre), and color change (6–9).

The protective efficiency of each product was evaluated by comparing the amount of water absorbed by capillarity according to the following formula:

$$(A1 - A2)/A1 \times 100,$$

where

A1 = water absorbed by the untreated sample at time t

A2 = water absorbed by the treated sample at time t

Results and discussion

Homopolymers of the fluorinated acrylic (XFDA) or methacrylic esters (TFEM, PFPM and XFDM), as well as their copolymers with nonfluorinated analogs (2-ethylhexylacrylate = EEA and methylmethacrylate = MA) were obtained by free radical polymerization with AIBN as initiator. The conversions obtained were in general rather high (70–90% by weight). In the case of TFEM, the use of different solvents and the variation of the molar ratio of monomer versus initiator allowed us to modulate the average molecular weight number between 4,000 and 43,000 and to a certain extent also molecular weight distribution, the dispersity index being between 1.7 and 3.5.

The flexibility of these fluorinated polymers was tested by measuring their glass transition temperatures (T_g). This T_g was only about 16°C higher than Paraloid B72; the molecular weight is comparable. It is of interest to note that T_g can be reduced by copolymerization (Table I).

Table I. Preparation of different polymers from trifluoroethyl alcohol and pentafluoropropyl alcohol methacrylic derivative.

Monomer (s)	Solvent	AIBN (wt%)	Conver- sion %	Mn $\times 10^3$	MWD index	T_g °C	Degrada- tion (T °C)
TFEM ^a	none	1	97	43	2.6	—	—
TFEM/EEA (1/1) ^a	none	1	93	—	—	—	—
TFEM ^b	dioxane	2	86	8	2.9	59.7	254/364
TFEM ^b	dioxane	6	80	4	3.5	—	—
TFEM/MA (2/1) ^c	dioxane	4	93	14.6	1.7	52.8	367.7
PFPM	CH ₃ CN	1	72	36	1.8	—	—
PARALOID B72	—	—	—	9.5	3.1	43.7	340

^a T = 60°C, t = 20 h.

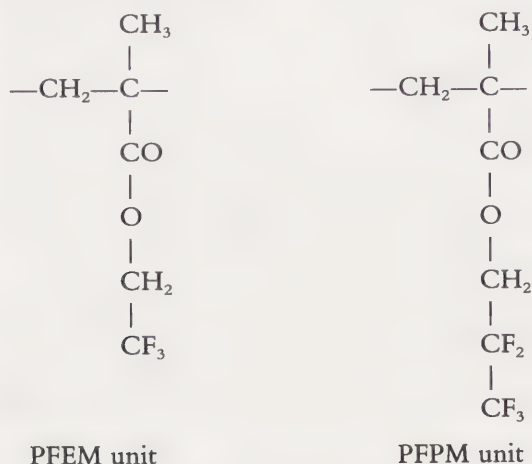
^b T = 60°C, t = 72 h.

^c T = 60°C, t = 72 h.

TFEM = trifluoroethylmethacrylate; EEA = 2-ethylhexylacrylate; MA = methylacrylate; PFPM = pentafluoropropylmethacrylate.

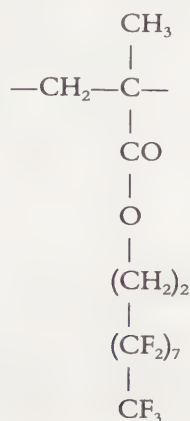
— = no data collected.

The polymers described in Table I are characterized by the presence of a trifluoromethyl group ($-\text{CF}_3$) in case of TFEM and a pentafluoroethyl group ($-\text{CF}_2\text{CF}_3$) in case of PFPM. Thus, for the corresponding monomeric unit the H/F ratio is 7/3 and 7/5 respectively.



The average H/F ratio and distribution of fluorinated side chain have been modulated by copolymerization. A substantially different structure can be obtained for monomers derived from perfluorodecyl alcohol (XFDA and XFDM).

In particular, for the methacrylic derivative XFDM, the H/F ratio in the monomeric unit is as low as 9/17.



XFDM unit

Thus, whereas the homopolymer is very slightly soluble and not easy processable, low T_g materials can be prepared by copolymerization with EEA, which still have a good H/F balance thanks to the long fluorinated side chain of XFDM (Table II).

Table II. Preparation of different polymers from perfluorodecyl acrylic derivatives.

Monomer (s)	Solvent	AIBN (wt%)	Conversion %	T _g °C
XFDA ^a	none	1	90	— ^b
XFDA ^a	dioxane	1	75	—
XFDM/MM				
(1/1) ^c	none	2	70	—
XFDM ^d	dioxane	2	90	— ^c
EEA ^d	dioxane	2	95	-71.1
XFDM/EEA ^d				
(1/5)	dioxane	2	90	-52.9
XFDM/EEA ^d				
(1/10)	dioxane	2	88	-58.9
XFDM/EEA ^d				
(1/15)	dioxane	2	89	-62.5

^a T = 65°C, t = 24 h.

^b Presence of degradation step at T = 352°C.

^c T = 70°C, t = 40 h.

^d T = 70°C, t = 120 h.

^e Presence of a melting band with T_f = 85.3°C and ΔH_f = 9.5 J/g XFDA = perfluorodecylacrylate; XFDM = perfluorodecylmethacrylate.

— = no data collected.

As reported in a previous paper the stability of the fluorinated acrylic polymers was checked by comparative FTIR analysis of freshly prepared and UV-irradiated samples as described in the experimental part (3). After 72 hrs the spectral changes observed for the polymers derived from TFEM and PFPM are similar to those for Paraloid B-66, B-67, B-72, and polymethylmethacrylate (PMMA) (10, 11).

However, while a comparable broadening of the (>C=O) absorption between 1650 and 1600 cm⁻¹ was observed in all cases, less evident variations were observed for the fluorinated polymers in the spectral region 3600–3300 cm⁻¹ (–OH groups), 3100–2800 cm⁻¹ (≧CH groups) and 1300–950 cm⁻¹ (≧C–O–C≡ groups). Moreover, spectral changes were observable already after 12 hrs for the nonfluorinated materials, compared to the 24 hrs for TFEM and PFPM polymers.

A preliminary evaluation of the protective behaviour of the fluorinated acrylic polymers was carried out by measuring water absorption, contact angle, and color changes in case of untreated and treated stone samples of different lithotypes

such as Carrara Marble, Vicenza Stone, and Verona Red (Table III) (12–14). Even if these data have to be considered only as indicative, they do, however, show some interesting features about the newly prepared side chain fluorinated polymethacrylates.

Table III. Evaluation of protective efficiency of poly(pentafluoropropylmethacrylate).

Sample	Water capillary absorption (mg/cm ²)		Contact angle	Variation color index (ΔE)
	1 h	48 h		
Carrara Marble				
A	7.95	8.60	—	—
B	0.45	2.29	99	2.0
C	0.33	7.85	81	1.8
Vicenza Stone				
A	399	451	—	—
B	903	153	103	9.4
C	220	421	81	7.5
Verona Red				
A	1.25	15.3	—	—
B	0.33	10.3	107	11.3
C	0.50	8.5	82	14.2

A = untreated; B = treated with PPFPM; C = treated with Paraloid B72; — = no data collected.

The most evident indications are supplied by the water absorption data at different times. Indeed, while at 1 hour from the treatment both PPFPM and Paraloid B-72 show a comparable and good impermeability with respect to the untreated material, after 48 hours the fluorinated polymer gives better performances, particularly in case of the Vicenza Stone, which has a rather high porosity.

The promising properties of PPFPM as stone protection material, at least as a good hydrorepellent, are substantiated by the values of the contact angle, which varies from 99 to 107° (from Carrara Marble to Verona Red), while with Paraloid B-72 values of only 81–82° are obtained for all lithotypes.

Variation of color index is substantially similar in all cases and suggests that some alteration of color has occurred in both PPFPM and Paraloid B-72 treated lithotypes, but these results need additional analysis before a conclusion can be drawn.

Final remarks

The objective of the present work was focused on the easy preparation of partially fluorinated polymers with good mechanical and stone protective properties. From the point of view of synthesis, the results described here clearly indicate that the chosen preparative approach offers good potential for modulating molecular structure. Indeed, the selection of the fluorinated alcohol used to prepare the methacrylic (or acrylic) ester, the copolymerization with non-fluorinated comonomers, and the use of different conditions allow to obtain material with variable fluorine content and distribution and rheological properties (average molecular weight and its dispersity), as well as flexibility of the derived films.

The evaluation of the stability and protective efficiency of the materials under examination has been only partial and indicative. The FTIR analysis after artificial weathering provides evidence that the partial substitution of H with fluorine in the side chains does not provide a complete stability, even if some improvement is observed with respect to non-fluorinated polymethacrylates or acrylates.

The tests on lithotypes are even more difficult to interpret in connection with polymer molecular structure, the nature of the stone playing a very determining

role. At present it is possible to conclude that the controlled substitution of specific hydrogen atoms with fluorine provides an efficient tool for improving and modifying the behaviour (in particular hydrorepellency) of newly designed polymers for stone protection. Further work is in progress and will be the subject of future publications.

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Abstract

A device has been developed for studying the effect of light on polymeric materials used in conservation (i.e. consolidants, adhesives, resins). The light source, standard fluorescent tubes with polycarbonate UV filters, is intended to approximate the spectral emission and spatial distribution experienced by objects in museums. The paper explains the development of the apparatus and provides schematic diagrams. Also described are the techniques for measurement and results obtained for light intensity, spatial and spectral distribution of light, and absolute irradiated energy in watt/cm². The usefulness of this apparatus is being evaluated with a study of the light stability of parylene.

Keywords

Parylene, UV, light stability, accelerated aging, polycarbonate

The Development of an Apparatus for Studying the Effect of Light Exposure on Museum Materials

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Introduction

The aim of this study was to produce an apparatus for exposing materials to moderately intense light (i.e. above ambient intensity) in order to accelerate the damaging effects for observation within a reasonable period. This was done as part of the CCI study on the use of parylene in museums. In developing this apparatus we hoped to estimate the effect of long-term exposure under lighting conditions that might actually be experienced by materials and objects in Canadian museums. The need for this apparatus was particularly evident with parylene because it has been shown to be sensitive to UV light (1). However, in Canadian museums where the use of UV-filtered light sources is widespread (its use is the norm in major museums), museum objects are exposed to very little UV radiation. It seemed to us, therefore, that use of light sources with a significant UV component could give misleading results. It is important to note that the presence of UV does not simply accelerate degradation; its effect is more subtle. Certain chemical species, such as carbonyl groups, that are involved in the degradation process may be degraded by UV light, but not by visible light. Other species such as peroxides may be decomposed by both visible and UV light. It is our contention that the UV component in light and the ratio of UV light to visible light must be taken into account when designing an aging apparatus.

It was immediately apparent that we had to develop our own apparatus since no commercial aging equipment was suitable. While there are many types available for conducting fading tests or weathering studies, the spectral distribution of the light sources employed—normally high wattage xenon arc lamps—is inappropriate, since they usually are intended to reproduce intense summer sunlight (N.B., filters are available to remove the UV component from xenon arc sources) (2). Other types of apparatus use high-pressure mercury lamps to yield an intense broad band in the UV region and clearly these extreme conditions are unlikely to relate to any museum (See reference 3 for a typical example). As suggested above, the use of fluorescent tubes screened (or filtered) by UV-absorbing polycarbonate sleeves has become common within museums in Canada although there are also many other forms of lighting, ranging from filtered daylight to tungsten filament spotlights. However, UV light has been largely eliminated within Canadian museums.

Most commercial aging equipment also has an unrealistic spatial distribution of light, and only irradiation that is normal to the surface of the material being tested is employed. This makes it easier to calculate and control the light intensity. However, diffuse lighting is more likely to be experienced by most objects in museums. An exception is the equipment described in ASTM designation D4674-89 which employs a curved array of fluorescent sunlamps (with a high UV component); the sunlamps have a curved reflecting rear surface that certainly provides diffuse lighting, however, the spectral emission of the lamps is unsuitable.

The apparatus we developed originated from a design originally conceived by Down and MacDonald (4). The following list summarizes our requirements for it:

- The apparatus should be able to handle a large number of samples.
- The samples should be easily accessible for analysis, and require a minimum of extraneous materials for support.

- The intensity of the light should be as even as possible over the sample platform surface.
- The light should be diffuse rather than directional.
- For transparent samples there should be minimal light reflected from the surface of the sample platform to return through the rear surface of the sample.
- The spectrum of the light should be as close as possible to realistic museum conditions. That is, there should be a minimal but not completely absent component of UV radiation. The Canadian Conservation Institute has established norms for the allowable lighting levels within museums and galleries (5). Thus, the UV component should not exceed 75 microwatts per lumen.
- The total energy, the spectral distribution, and the spatial distribution of the light should be known, and where applicable, monitored against time.
- There should be good ventilation, and the temperature and relative humidity should remain close to ambient.
- The materials of construction should be stable and release a minimal amount of volatile contaminants.
- The apparatus should be approved for electrical safety.

Once equipment is designed, it can only be tested and subsequently modified if there are precise measurements of the emitted light. There are some problems in using the light monitoring equipment recommended for museums (6). While the luxmeter is a useful instrument for monitoring museum lighting, it is not accurate enough for determining the exposure conditions in a scientific experiment. The reading given by a luxmeter depends on built-in assumptions about the spatial and spectral distribution of light. The meter could give major differences in readings for the same intensity if the light is diffuse or direct or if the spectral distribution (colour temperature) differs from tungsten light. Proper photometric and spectral measurements have to be made.

To characterize exposure conditions properly it is necessary to know:

- 1) The spectral distribution of light
- 2) The spatial distribution of light
- 3) The absolute energy of light
- 4) How the emission changes with time

We obtained this information using a calibrated photometer, interference filters of known performance, and a monochromator.

Experimental

Basic considerations for the experiment

The light source originally consisted of an array of 16 40-watt, 4-foot 1157 Vita-lite fluorescent tubes. The number of tubes was later reduced to 14 tubes. The light is filtered with polycarbonate filters that sheathe the fluorescent tubes. The polycarbonate has a cut-off at 382 nm which attenuates, but does not completely eliminate UV light.

Construction of the light rack

The design is shown in Figure 1. To save space, the rack was built with the sample platform almost vertical. For access, the platform hinges back. When in place, the sample platform is inclined back at about 10° from the vertical in order to simplify sample attachment. From earlier measurements, we knew that using a row of fluorescent tubes to create intense light had a number of problems. Intensity at the platform surface tended to be very uneven with a high intensity at the centre and a lower intensity towards the edges. To minimize this problem the rack had adjustable geometry. After some trial and error, the fluorescent tubes were adjusted to be further from the sample platform at the centre and the tubes were thus arranged in an arc formation.

The frame was of Dexion and the sample platform was constructed of a 2.4 × 1.2 m rigid panel of 1.25-cm thick, medium density overlaid plywood with a surface of black non-reflective Coroplast. The apparatus was further modified

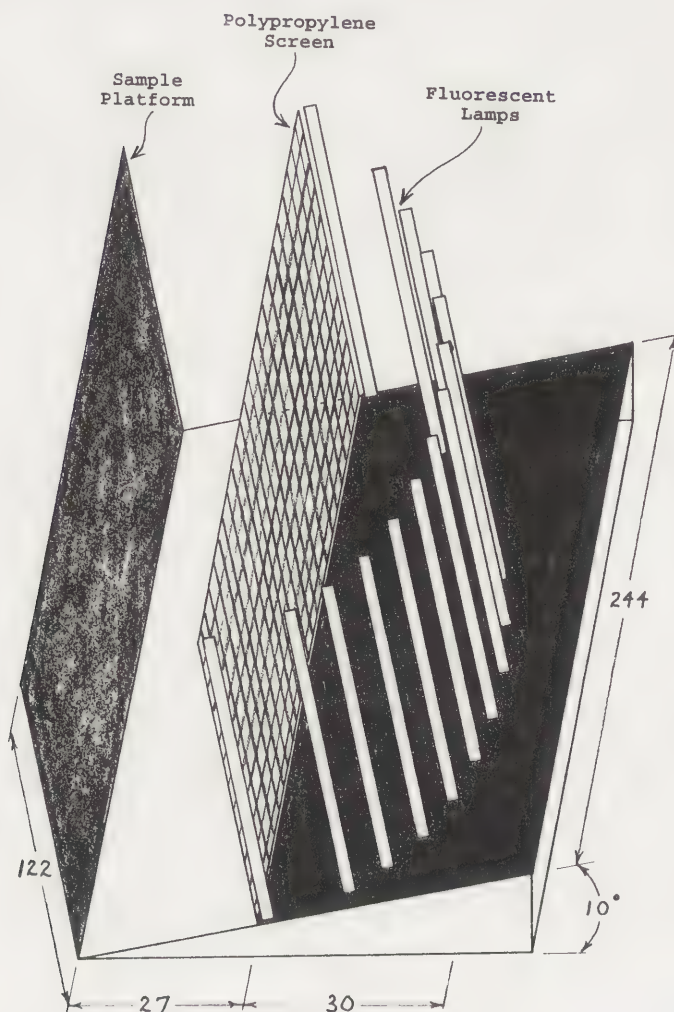


Figure 1. General arrangement of light rack.

by covering the Coroplast with black velvet to reduce rear reflections. Electrical wiring was 14/3 type SJ wire rated at 600°C.

Light measurement

For surveying intensity distribution at the sample platform surface, an Optikon model EC1 luxmeter was used. This has a silicon photodiode sensor and a range of 1 to 200,000 lux.

For making precise light measurements (in watts/cm²), a research radiometer (International Light model IL 1700) in combination with a light sensor (International Light model SED 038) was used. This has a silicon detector with a quartz window, a spectral range of 200 to 1100 nm, and a dynamic range 5×10^{-11} to 1×10^{-2} watts/cm². The efficiency distribution of this detector is shown in Figure 2. For measurement of the total energy, the SED 038 sensor was mounted flush with the surface of the sample platform.

A light collimating tube was constructed to enable the measurement of spatial distribution and to use with interference filters, which function most efficiently with light directed normal to the surface. The light collimating tube was built from ABS pipe and is shown in Figure 3. It has internal baffles which restrict the deviation of incident light striking the interference filters to less than 3.5° from normal; the baffles also prevent internal reflections. This means that transmitted light is at maximum 0.26 nm different from the stated wavelength of the filter. For measurements of angular distribution and use of the interference filters, the SED 038 light sensor was mounted at the base of the collimating tube.

The tube was arranged so that the open end was flush with the surface of the sample platform, and was attached to a device which allowed it to be oriented

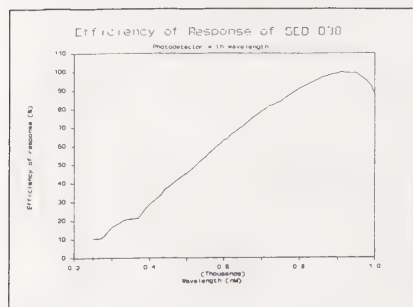


Figure 2. Efficiency of response of International Light Sensor 038 versus wavelength from 200 to 1000nm.

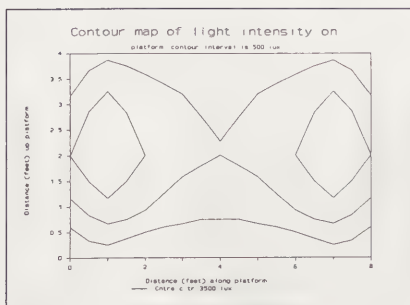
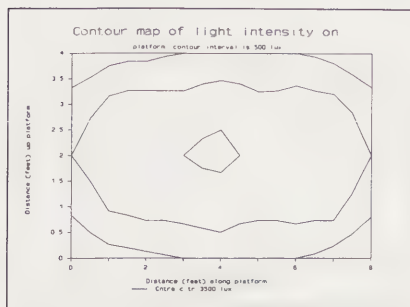
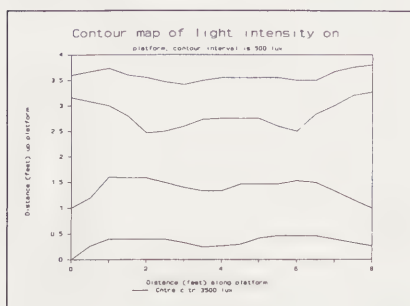
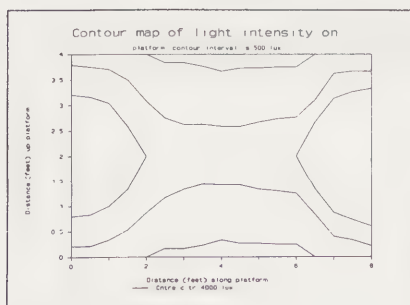


Figure 4. Light Intensity variation at the sample platform surface for the unmodified apparatus (contour interval 500 lux). The central contours are at 3500 lux.



Figures 5–7. Light Intensity variation at the sample platform surface, showing the effect of modifying apparatus (contour interval 500 lux). The central contours are at 4000, 3500, and 3500 lux, respectively.

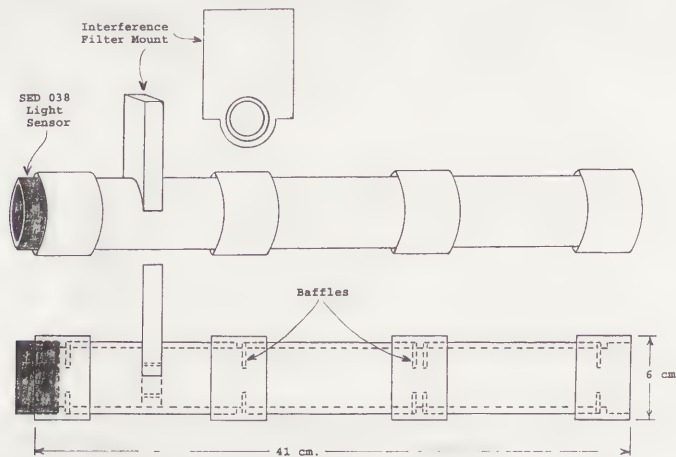


Figure 3. General arrangement of light collimating tube.

at different angles in the horizontal mode (i.e., perpendicular to the fluorescent tubes) or the vertical, but still with the open end flush with the surface.

Interference filters were obtained from Ealing Scientific Ltd. Those filters transmitting in the visible region have a nominal 10-nm bandpass, while those in the UV region have a 20-nm bandpass. The maximum transmission of the 17 filters occur is as follows: 260, 300, 340, 360, 380, 400, 450, 488, 500, 530, 550, 589, 600, 633, 650, 656, and 700 nm. A calibration plot for the transmission of each filter was supplied by Ealing Optical, and confirmed by spectroscopic measurement.

The monochromator was some years old, and was made by Bausch and Lomb but marketed by Gamma Scientific, Inc. as model 700-31. Its range is 330–830 nm. The wavelength calibration was checked by means of the interference filters.

Results, development, and discussion

Light intensity variation over sample platform surface

The initial arrangement of the light rack with the fluorescent tubes gave an intensity distribution shown in Figure 4. This was not considered satisfactory because the intensity declined badly at the edges and there was also a higher intensity zone at each end. To compensate for these defects, reflecting surfaces were added at the edges of the rack. The effect of this modification, which is shown in Figure 5, was to yield more intense lighting at the edges and, unfortunately, a region of lower intensity at the centre. To compensate for this unevenness in intensity, a fluorescent tube was removed from each end of the array (numbers 2 and 15) so that the number of tubes decreased from 16 to 14. As shown in Figure 6, this modified arrangement produced a 10% variation in intensity over 75% of the sample platform which we considered as usable.

Spatial distribution of light

The spatial distribution of the light was measured at the centre of the sample platform by moving the collimating tube and sensor assembly described previously through 180° horizontally and then vertically. Horizontally, the distribution was very uneven as is shown in the top curve in Figure 8. Maxima in intensity occurred when the sensor assembly pointed directly at fluorescent tubes and minima were observed when it was aimed towards the spaces between tubes. The vertical distribution is shown as the lower curve in Figure 9.

These spatial distributions were considered unsatisfactory for two reasons. Taken together they were a poor model for the diffuse lighting likely to be experienced by a museum object. Secondly, the differences between horizontal and vertical distributions and the angular variation in intensity made calculation of the total energy at the platform surface difficult. For this calculation, it is necessary to integrate the light falling on a particular element of the surface through all space.

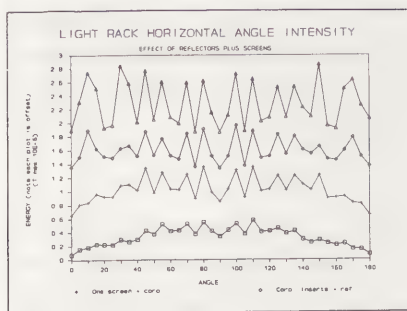


Figure 8. Spatial distribution of light at platform centre: horizontal mode from 0 to 180°. The top curve is with unmodified apparatus, and the lowest curve is after final modification with reflectors and screening. The vertical axes have been displaced to improve clarity.

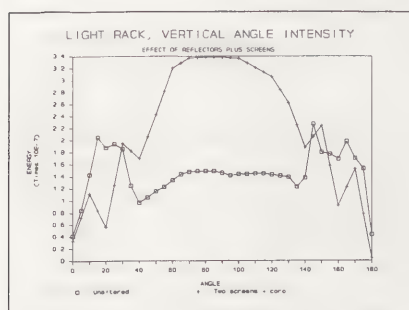


Figure 9. Spatial distribution of light at platform centre: vertical mode from 0 to 180°. The top curve is with unmodified apparatus, and the lowest curve is after final modification with reflectors and screening.

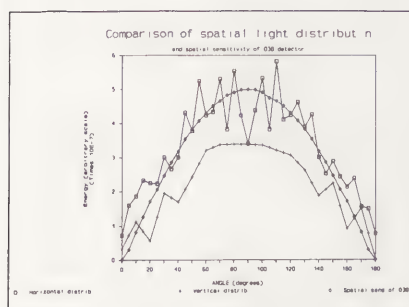


Figure 10. Spatial distribution of light from 0 to 180° compared with spatial response of the 038 sensor. The lowest curve (crosses) is the vertical distribution, the upper sawtooth curve (squares) is the horizontal distribution, and the upper smooth curve (lozenges) is the spatial sensitivity of the detector.

To overcome these problems white Coroplast reflector strips were inserted between the lights; first, one screen mesh baffle and then two were inserted between the lights and the sample platform. The effect of these measures is shown in Figures 8 and 9. In Figure 8, gradually improving horizontal distributions are shown (i.e., going from the top to the bottom curve. (Note that the curves have been offset vertically for ease of reading.) The lowest curve shows the final arrangement. In Figure 9, which shows the vertical spatial distribution, only the initial and final curves are shown. The upper curve, which represents the final arrangement, shows a much more even spatial distribution with a more pronounced maximum in light intensity normal to the surface.

Fortunately, these changes did not affect the light intensity distribution over the surface of the sample platform as measured by the luxmeter. The final result is shown in Figure 7.

Calculating the energy for spatial sensitivity of the detector

The light registered by the sensor is the product of its spatial response and the spatial distribution of the light. These are compared in Figure 10, in which the smooth curve is the response of the detector. The products of spatial distribution and detector response are shown for the horizontal and vertical modes respectively in Figures 11 and 12. In these, the product curves are compared with the actual light distributions. The ratio of the detector reading to the actual energy is given by ratio of the areas beneath the product curves to that beneath the spatial distribution curve. This reveals that 73.6% of the horizontal light and 77.0% of the vertical light is registered by the detector at the centre of the sample platform. The distributions are similar to one another, and it can thus be reasonably assumed that their average, 75.3%, is a good approximation of the efficiency of light measurement over all space. Thus to get the spatially corrected energy from the SED 038 detector readings, the measured value must be multiplied by 100/75.3.

Calculating the energy for spectral distribution of the light

To measure the spectral distribution, it is necessary to have some form of calibrated intensity measurements of light at various wavelengths over the emission spectrum. We accomplished this by using a series of interference filters of known cut-off in wavelength and known efficiency to enable measurement of absolute intensity at given wavelengths. The results are shown in Figure 13.

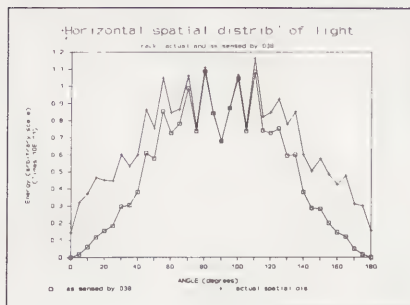
A monochromator was also used to scan the light emitted by the fluorescent tubes. Figure 13 shows the comparison of spectra produced by the interference filters and the monochromator. The agreement is very good, and this is shown particularly by a plot of the ratio of the two curves in Figure 13. The one divergent part is the UV region where it appears that the monochromator transmits less light than the interference filters. In this region, the ratio of the monochromator transmittance to the interference filter transmittance increases markedly.

For the purposes of calculation of overall energy, this small difference is not serious. However, the monitoring of the UV component could be a problem and thus the interference filter is a better indicator of UV light.

Overall energy registered by the detector can be calculated by comparing the area beneath the uncorrected spectral emission with that of the curve corrected for the variation in efficiency of response of the sensor (as shown in Figure 2) with wavelength. This is shown in Figure 14. In this it was found that the uncorrected area is 1.48 times less than the corrected area. Thus, the output from the detector must be multiplied by a factor of 1.48 to compensate for spectral distribution *with this and only this light source* and the variation in the efficiency of the sensor with wavelength.

Spatial and wavelength correction for the International Light 038 sensor

To correct for non-uniform spatial sensitivity and non-uniform wavelength sensitivity, the sensor output must be multiplied by $1.48 \times 100/75.3 = 1.97$.



Figures 11. The spatial distribution of light from 0 to 180°. The lower curve, the product of the spatial distribution and the spacial sensitivity of the detector, is an indication of what the sensor actually senses and how it differs from irradiated light which is shown in the upper curve.

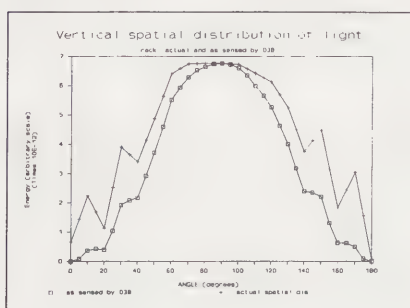


Figure 12. The spatial distribution of light as described in the legend to figure 11, but for the vertical mode.

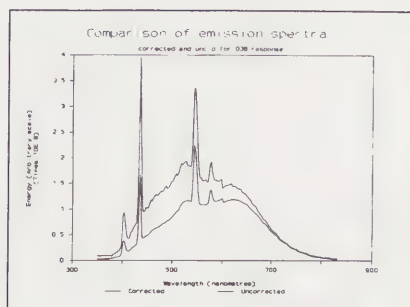


Figure 14. The emission spectrum corrected (upper curve) and uncorrected for the response of the 038 sensor.

On June 13, 1991, the detector reading was 6.90×10^{-4} watts per cm^2 . When corrected, this reading becomes 13.8×10^{-4} watts per cm^2 . Readings that were corrected 30 cm to the right and left were 13.6 and 13.3×10^{-4} watts per cm^2 , respectively.

Reflection measurements

There was concern that though black Coroplast was used as a sample platform, light could be reflected back and thus the measured light intensity may not indicate the actual exposure. Using a reflection meter and also monitoring the reflected light from diffusely illuminated Coroplast, it was found that when the angle of reflection went from 30° through normal to 120°, 10% of the light was reflected back in this region. At shallower reflection angles (i.e. <30° or >120°), the efficiency increased to about 40%. This was considered unacceptable because it would increase illuminated intensity by about 10%. It was thus decided to cover the Coroplast with a layer of black velvet for which the reflection was almost negligible.

Variation with time

The characteristics of fluorescent tubes and also of polycarbonate filters change with time as they age. Thus, it is necessary to monitor these changes to determine exposure conditions. This has been achieved by measuring the total energy in five locations (at the centre, top, bottom, right edge, and left edge) on the sample platform, and by repeating the scan of the emission spectrum. This was done for the December 1990 and June 1991 readings (See fig. 15). On December 1990, the intensity was 15.4×10^{-4} watts per cm^2 , and by June 13, 1991, the intensity declined to 13.8×10^{-4} watts per cm^2 . In the final six months of 1992, it stabilized to 12.6×10^{-4} watts per cm^2 . Notice in Figure 15 that the ratio of one emission spectrum to the other is also plotted. If there is no change in spectral distribution, then the ratio of these intensities at different wavelengths should be constant. This should be evident if the ratio appears as a horizontal straight line. In the central region, a horizontal plot was observed. However, in the UV region the ratio became non-linear and it declined in the UV region. This indicated that less UV light was being emitted as the system aged.

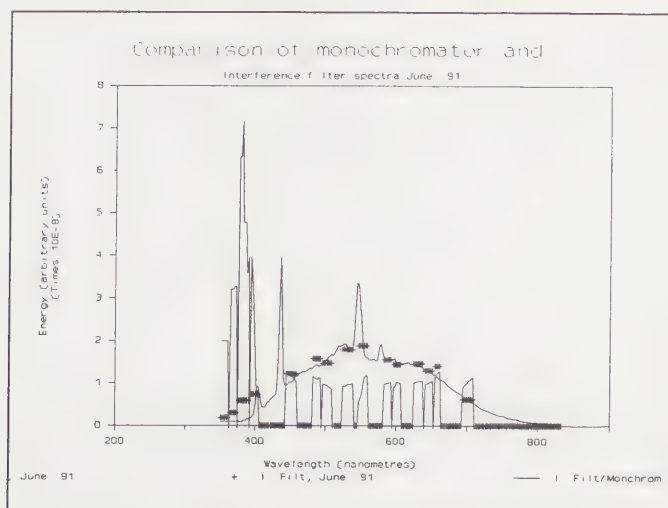


Figure 13. The emission spectrum of light as given by the monochromator with the 038 sensor (upper continuous curve). The crosses are the energy (i.e., spectrum) as recorded using the interference filters with the 038 sensor. The lower continuous curve is the ratio of the energy as recorded by interference filter, etc., over that recorded by the monochromator, etc.

Comparison with other work

It is to be hoped that others will adopt similarly precise methods of measuring lighting conditions, rather than relying on lux readings. Unfortunately, this is

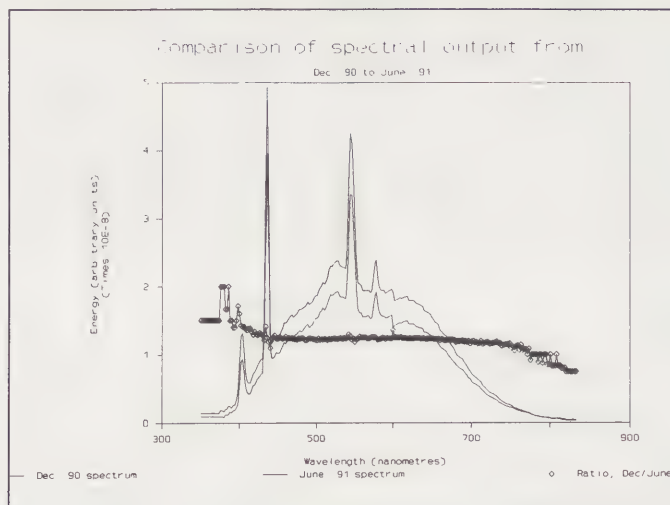


Figure 15. The decline in energy after six months. The upper curve shows the initial emission spectrum. The approximately horizontal curve parallel to the wavelength axis (diamond shaped points) is the ratio of the initial spectrum divided by the spectrum after six months. There is an overall decline in intensity, which is greatest in the UV region (< 420 nm) and least at the red end of the spectrum (> 730 nm).

not yet the case in conservation although these type of precise methods have been used in other fields, such as the study of plastics degradation, for some time. At present, we were unable to compare our data with others so, with some degree of reluctance, we introduced Blue wool standards to enable some comparison with other exposure conditions. In the opinion of the authors, any such comparisons are highly questionable.

Conclusion

The light irradiation apparatus has been used successfully for some time. The absolute intensity continues to decline as the fluorescent lights age, although the spectral distribution has now stabilized. We realize that the apparatus described is far from perfect, but we hope that the work and ideas expressed here stimulate other attempts to construct light-aging equipment and also to report lighting in terms of absolute energy, spatial distribution, and spectral distribution.

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Abstract

Polymer additives for synthetic low-molecular-weight picture varnishes are described. These may modify rheological properties of the varnishes, the appearance that can be obtained with them and the brittleness of the dry films. Styrene-ethylenebutylene-styrene rubbers and a hydrogenated polyisoprene rubber were added at 10% to hydrogenated hydrocarbon resins. Poly (n-butyl methacrylate) was added at 10% to an aldehyde resin. Long-term aging in a xenon arc Weatherometer of films of the low-molecular-weight resins as well as of films of low-molecular-weight resin/polymer mixtures indicates that they are stable when a hindered amine light stabilizer is incorporated. No insolubility caused by crosslinking appears to occur in these films.

Keywords

Picture varnish, coating, hydrogenated hydrocarbon resin, aldehyde resin, styrene-ethylenebutylene-styrene copolymer, hydrogenated polyisoprene, poly (butyl methacrylate), stability, cross-linking, accelerated aging

Polymer Additives for Synthetic Low-Molecular-Weight Varnishes

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Introduction

Hydrogenated hydrocarbon (HHC) resins and an aldehyde resin are synthetic low-molecular-weight (LMW) resins that have been recently introduced for use in picture varnishes [1]. These resins are considerably more stable than natural resins and ketone resins, LMW resins commonly used in varnishes. Using varnishes containing synthetic LMW resins, an appearance comparable to that achieved with a dammar or mastic varnish may be obtained [2,3]. Good results with these products have been reported [4] and practical methods for obtaining the desired appearance have been described [2]. There are some reports, however, that synthetic LMW varnishes can be too glossy, that it may be hard to control the gloss or that the varnish may be absorbed by porous paint layers [4].

Not all requirements of a coating may be obtained using a single solid ingredient [5]. Dammar resin and gum mastic have complex compositions, that are only known in part. Commercial coatings usually contain a number of ingredients, each with their own function. Although it is generally recommended to keep the composition of conservation materials simple, it is worthwhile to consider the benefits of some additives. Stabilizing additives, for example, can play an important role. Other additives have the potential of modifying the rheological properties of resin solutions as well as the mechanical and adhesive properties of the coatings obtained with them. Although the main fractions of dammar resin and gum mastic are monomeric with molecular weights in the 400–500 range, a small but significant polymeric fraction is present. It is likely that the polymeric fractions of dammar and mastic play a role in the rheological properties of their solutions and in the appearance that can be obtained with them. One obvious benefit of addition of some polymer to synthetic LMW coatings will be reduction of their inherent brittleness. It was decided, therefore, to investigate the effects of polymeric additives on synthetic LMW coatings.

In this paper, results of accelerated aging of varnish films are reported. Mechanical and other physical tests, such as determination of glass transition temperatures, are underway and will be the subject of future publications. Films were aged for a longer period than that used in the previous study [1] and tests for the development of insoluble material were added to the measurements. Films of synthetic LMW resins and of synthetic LMW resin/polymer mixtures were tested. For comparison, some data for dammar resin, Laropal K80 (ketone resin; BASF) and MS2A (chemically reduced ketone resin; Laporte) are included.

Materials and methods

The materials tested are listed in Table I. Three synthetic LMW resins, the HHC resins Arkon P90 (Arakawa) and Regalrez 1094 (Hercules), and an aldehyde resin (BASF) were used for this study. The aldehyde resin is an experimental condensation product of urea and low molecular weight aldehydes, that is not commercially available [1].

The compatibility of materials was tested by dissolving LMW resins in an appropriate hydrocarbon solvent and adding polymer at concentrations of 5 and 10%. Polymers were considered compatible with the LMW resin if a single phase occurred.

An important requirement of a picture varnish is solubility in a hydrocarbon solvent of low aromaticity, such as mineral spirits. Few synthetic polymers exist that meet this requirement. Among those that do are synthetic rubbers, such as Kraton rubbers (Shell), which were found to be compatible with HHC resins but not with the aldehyde resin. Poly (alkyl methacrylates) in which the alkyl

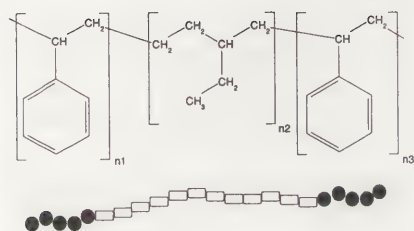
Table I. Synthetic low-molecular-weight (LMW) resins and polymers tested.

LMW resin	Supplier	Type
Arkon P90	Arakawa	Hydrogenated hydrocarbon resin
Regalrez 1094	Hercules	Hydrogenated hydrocarbon resin
Aldehyde resin	BASF	Urea-aldehyde condensation product

Polymer	Supplier	Type*	% Styrene**	Viscosity**
Kraton G1650	Shell	S-EB-S	29	8000
Kraton G1652	Shell	S-EB-S	29	1350
Kraton G1657	Shell	S-EB-S	13	4200
Kraton G1726	Shell	S-EB-S	30	200
Kraton G1750	Shell	HPI	N/A	(high)
Elvacite 2044	Du Pont	PBM	N/A	

* S-EB-S = styrene-ethylenebutylene-styrene block copolymer; HPI = hydrogenated polyisoprene; PBM = poly (n-butyl methacrylate).

** Data from Shell; viscosity = Brookfield viscosity in toluene at 25°C (centipoise).



1. Structure of Kraton styrene-ethylenebutylene-styrene (S-EB-S) block copolymers.

group has four or more carbons are also soluble in mineral spirits. Poly (butyl methacrylates), such as Elvacite 2044, Elvacite 2045 (Du Pont) and Acryloid B67 (Rohm and Haas), were found to be compatible with the aldehyde resin. All mixtures are soluble in Shell mineral spirits 135, which is 15% aromatic [1].

Kraton G1750 is hydrogenated polyisoprene [6]. The other Kraton products are styrene-ethylenebutylene-styrene (S-EB-S) block copolymers of varying molecular weight and hence viscosity (see Table I and Figure 1). The mid block of the S-EB-S copolymers is a saturated elastomer, making them more resistant to oxidative degradation than unsaturated rubbers. The styrene end blocks form physical bonds, resulting in a network which gives the polymer strength. Because the bonds are physical rather than chemical, they are reversible [7].

Elvacite 2044 is an n-butyl methacrylate homopolymer. It was chosen because it is softer and has a lower crosslinking rate than poly (i-butyl methacrylate) (such as Elvacite 2045 and Acryloid B67). Films of poly (butyl methacrylates) are known to become completely insoluble due to crosslinking when exposed to (UV) light [8,9] and they should not be used, therefore, as the major ingredient of a varnish. However, it was anticipated that crosslinking is insignificant when the polymer is a minor component of the varnish.

All products were tested as films cast from solutions in reagent grade toluene. Polymers were added to LMW resins at a concentration of 10% of the weight of the LMW resin. Unstabilized films as well as films containing the hindered amine light stabilizer (HALS) Tinuvin 292 (Ciba-Geigy) were tested. The concentrations of Tinuvin 292 used are indicated in percent of the combined resin weight. The films were allowed to dry at room temperature for about two weeks and then aged in an Atlas xenon arc Weather-ometer in which daylight through window glass is simulated (including the UV component).

Fourier-transform infrared (FTIR) spectra were recorded of films cast on reflecting plates. Solubility tests using cotton swabs and cyclohexane/toluene and toluene/acetone mixtures were carried out on films cast on glass plates. More accurate determinations of the amount of insoluble material were also carried out. The results of the cotton swab tests are referred to as removability in order to distinguish them from tests for insoluble material. Further experimental details are given in the Experimental section.

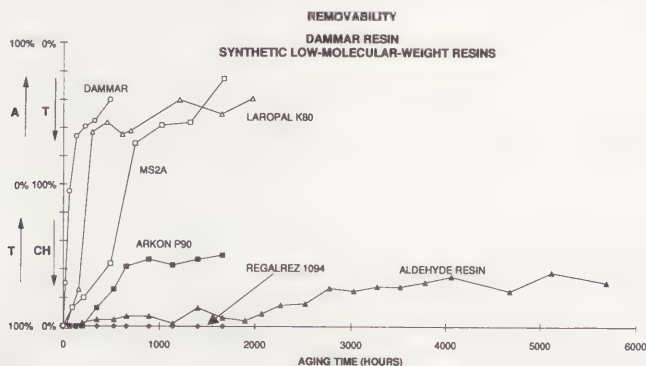
Results

Synthetic low-molecular-weight resins

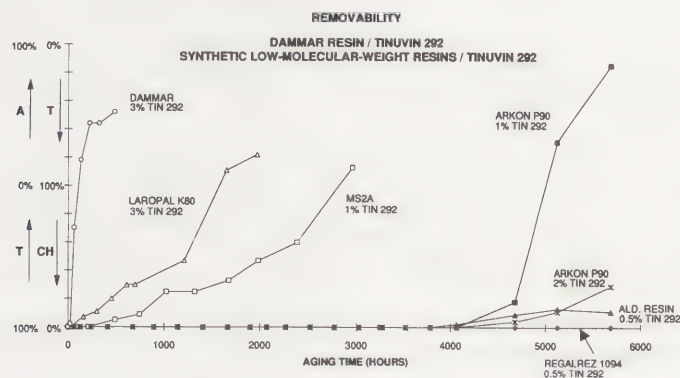
Removability

All films are removable with 100% cyclohexane when fresh. Upon aging the polarity of the resins increases as a result of formation of species containing ketone, hydroxyl and carboxylic acid groups, and the films require more polar

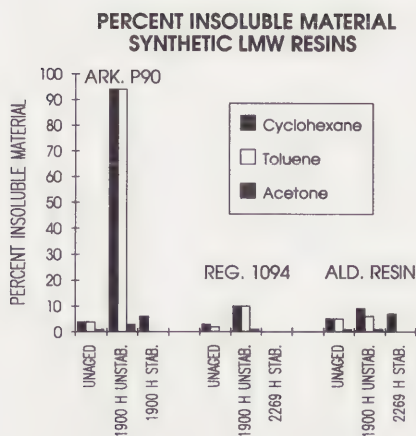
solvents for removal. The results of removability measurements of films aged in the Weather-ometer up to almost 6000 hours appear in Figures 2a and 2b.



2a. Removability of films of unstabilized dammar resin and synthetic low-molecular-weight resins during aging in a xenon arc Weather-ometer. Data points indicate the least polar solvent mixture with which the film can be removed, using toluene (T)/cyclohexane (CH) and acetone (A)/toluene (T) mixtures.



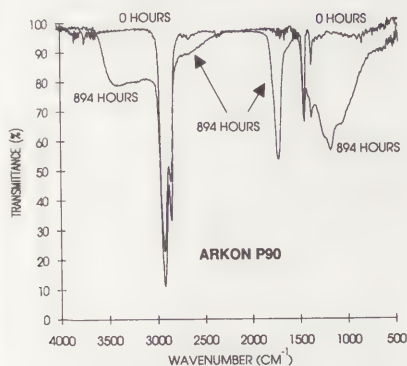
2b. Removability of films of dammar resin and synthetic low-molecular-weight resins stabilized with Tinuvin 292 during aging in a xenon arc Weather-ometer. Data points indicate the least polar solvent mixture with which the film can be removed, using toluene (T)/cyclohexane (CH) and acetone (A)/toluene (T) mixtures.



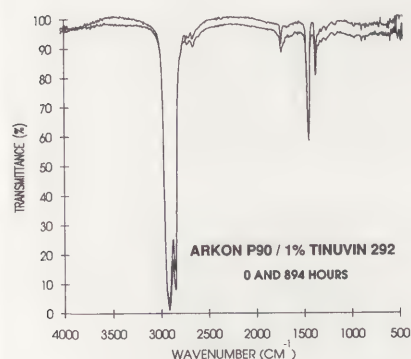
3. Percent material insoluble in cyclohexane, toluene and acetone in unaged films and unstabilized and stabilized Weather-ometer-aged films of synthetic low-molecular-weight (LMW) resins. Films were aged for the number of hours indicated in the figure. Arkon P90 films were stabilized with 1% Tinuvin 292 and Regalrez 1094 and aldehyde resin films with 0.5% Tinuvin 292.

Figure 2a shows removability for films of unstabilized dammar resin and synthetic LMW resins. Dammar, Laropal K80 and MS2A show dramatic changes in removability in the first few hundred hours of aging, after which they require about 50/50 acetone/toluene. The two HHC resins and the aldehyde resin remain removable in a solvent mixture that is not "stronger" than 50/50 toluene/cyclohexane. However, both HHC resins were severely embrittled after 1700–1900 hours and the aging was terminated. The film of unstabilized aldehyde resin lasted without notable embrittlement for the duration of the experiment.

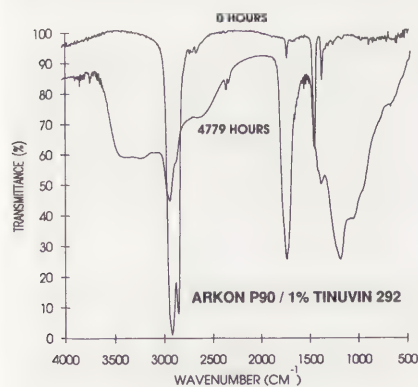
Figure 2b shows removability data for films of the same resins containing various concentrations of Tinuvin 292. It is clear from the figure that dammar is not stabilized by the addition of 3% Tinuvin 292 under these conditions [10]. Dammar can be stabilized effectively, however, when UV radiation below 400 nm is filtered out [10,11]. Laropal K80 is not stabilized significantly, even at an additive concentration of 3%. MS2A is stabilized to some extent with 1% additive, but the induction period (the period during which no changes occur) is very short (ca. 200 hours). Possibly, at 2% additive concentration a better stabilization is achievable. Both HHC resins and the aldehyde resin are stabilized significantly by Tinuvin 292. Regalrez 1094 and the aldehyde resin containing 0.5% of the stabilizer remain removable in toluene/cyclohexane mixtures that contain only a few percent toluene for the duration of the experiment. Arkon P90 is clearly the least stable of the three, as a film containing 1% Tinuvin 292 starts to change after ca. 4000 hours. A film containing 2% of the additive remains stable for a longer time. Interestingly, Arkon P90 stabilized with 1% Tinuvin 292, becomes more polar than the unstabilized product. This may



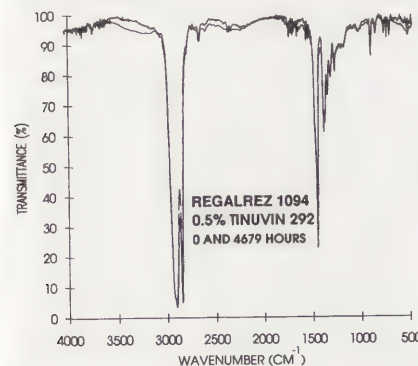
4a. Infrared spectra of a film of unstabilized Arkon P90 before and after aging for 894 hours in a xenon arc Weather-ometer.



4b. Infrared spectra of a film of Arkon P90 stabilized with 1% Tinuvin 292 before and after aging for 894 hours in a xenon arc Weather-ometer.



4c. Infrared spectra of a film of Arkon P90 stabilized with 1% Tinuvin 292 before and after aging for 4679 hours in a xenon arc Weather-ometer.



4d. Infrared spectra of a film of Regalrez 1094 stabilized with 0.5% Tinuvin 292 before and after aging for 4679 hours in a xenon arc Weather-ometer.

indicate that degradation in the stabilized resin follows a path different from that in the unstabilized resin.

Tests for insoluble material

Insolubility as a result of crosslinking reactions, such as occur in poly (butyl methacrylates), is unlikely in these LMW resins [9]. Nevertheless, tests for the occurrence of insoluble material were undertaken. Figure 3 shows the percentage of material insoluble in cyclohexane, toluene and acetone occurring in films of the HHC resins and the aldehyde resin before and after accelerated aging. Although the unstabilized Arkon P90 film is more than 90% insoluble in cyclohexane and toluene after 1900 hours of aging, it is almost completely soluble in acetone. This indicates that the resin is oxidizing but that no completely insoluble network is formed. A film of Arkon P90 containing 1% Tinuvin 292 develops a small amount of material insoluble in cyclohexane in 1900 hours of aging, but is completely soluble in toluene and acetone. Figure 3 also shows that no insolubility caused by crosslinking occurs in unstabilized Regalrez 1094 and the aldehyde resin after 1900 hours of aging and in the stabilized products containing 0.5% Tinuvin 292 after 2269 hours of aging. The figure illustrates the remarkable stability of these products compared to Arkon P90. Although measurements still have to be done after longer aging times, it appears that no insoluble material will be formed in these resins as a result of crosslinking reactions.

FTIR

The development of carbonyl, hydroxyl and carboxylic acid groups as a result of oxidation can be observed particularly well in the IR spectra of HHC resins which have no such groups before aging. Some of the FTIR spectra obtained on films of HHC resins appear in Figures 4a–d. Oxidation leads to a broad absorption band between approximately 3500 and 2500 cm⁻¹ (hydroxyl and carboxylic acid groups), an absorption band around 1700 cm⁻¹ (carbonyl groups) and absorption in the fingerprint region (<1300 cm⁻¹). Figure 4a shows the change in the IR spectrum of a film of Arkon P90 after 894 hours of aging. Figure 4b shows that no significant change occurs during the same period of aging in a film of Arkon P90 containing 1% Tinuvin 292. However, Figure 4c shows that the film containing 1% of the stabilizer is severely degraded after 4679 hours. Figure 4d illustrates the remarkable stability of a film of Regalrez 1094 containing only 0.5% Tinuvin 292, which shows virtually no change after 4679 hours of aging.

A carbonyl index was calculated using the formula:

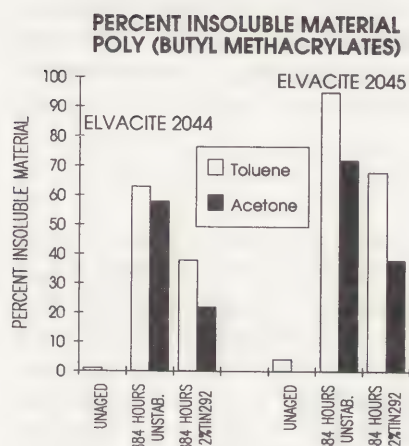
$$\text{C.I.} = 100 \times \{[A(1710,t) - A(2225,t)] - [A(1710,0) - A(2225,0)]\}/d$$

where $A(1710,t)$ is the absorbance at 1710 cm⁻¹ and aging time t in hours, and d is the thickness of the film in microns. Plots of the carbonyl index against aging time appear in Figure 5. Again, the outstanding stability of Regalrez 1094 is evident.

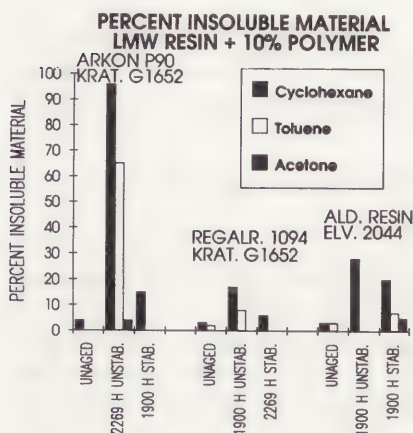
Mixtures of synthetic low-molecular-weight resins and polymers

Removability

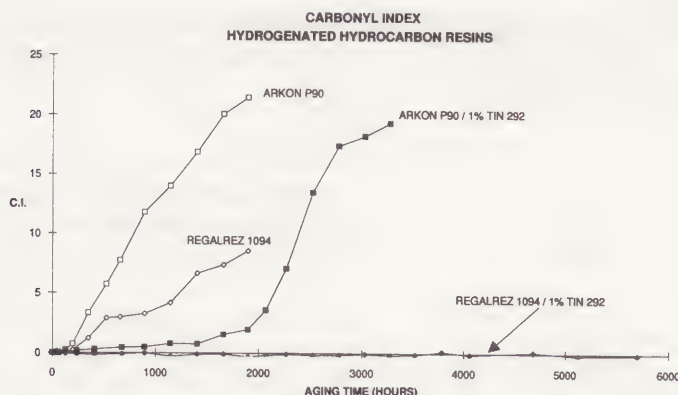
Figure 6 shows removability data for films of mixtures of LMW resins and polymers, with a polymer concentration of 10%, during accelerated aging for almost 6000 hours. Data for Arkon P90/Kraton G1650, Regalrez 1094/Kraton G1650 and aldehyde resin/Elvacite 2044 as well as data for the same mixtures containing 2% Tinuvin 292 are shown. The Arkon P90/Kraton G1650 combination is the least stable and develops a significant change in removability in the first 2000 hours, eventually requiring 100% acetone. The Regalrez 1094/Kraton G1650 combination remains soluble in 100% cyclohexane for about 2000 hours and then becomes more polar, also eventually requiring 100% acetone. The aldehyde resin/Elvacite 2044 combination starts to change gradually after about 300 hours but never becomes very polar. When stabilized with 2% Tinuvin 292, the Arkon P90/Kraton G1650 combination remains removable in 100% cyclohexane until about 4500 hours, after which a gradual change occurs. The Regalrez 1094/Kraton 1650 combination and the aldehyde resin/



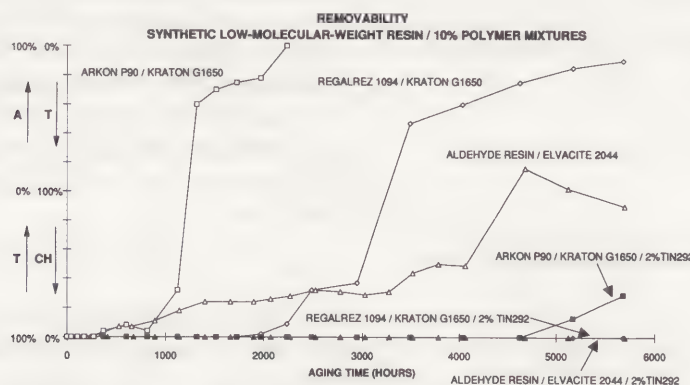
7a. Percent material insoluble in toluene and acetone in unaged films and unstabilized and stabilized Weather-ometer-aged films of poly (n-butyl methacrylate) (Elvacite 2044) and poly (i-butyl methacrylate) (Elvacite 2045). Films were aged for 884 hours. Stabilized films contained 2% Tinuvin 292.



7b. Percent material insoluble in cyclohexane, toluene and acetone in unaged films and unstabilized and stabilized Weather-ometer-aged films of synthetic low-molecular-weight (LMW) resin/10% polymer mixtures. Films were aged for the number of hours indicated in the figure. Stabilized films contained 2% Tinuvin 292.



5. Carbonyl index of films of unstabilized and stabilized hydrogenated hydrocarbon resins during aging in a xenon arc Weather-ometer.



6. Removability of films of unstabilized and stabilized synthetic low-molecular-weight resin/10% polymer mixtures during aging in a xenon arc Weather-ometer. Data points indicate the least polar solvent mixture with which the film can be removed, using toluene (T)/cyclohexane (CH) and acetone (A)/toluene (T) mixtures.

Elvacite 2044 combination remain removable with 100% cyclohexane for the duration of the experiment. Arkon P90 and Regalrez 1094 combined with other Kraton G series rubbers behave similarly, however, unstabilized films containing Kraton G1652 and G1726 are embrittled after 1700–1900 hours of aging and the aging was terminated.

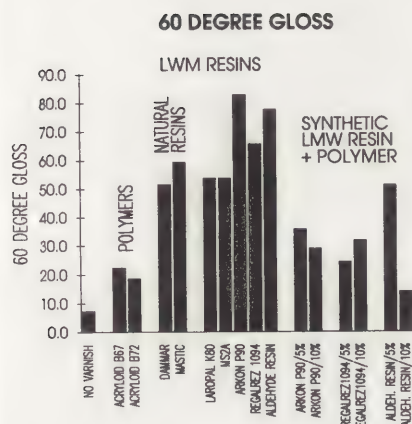
Tests for insoluble material

The effect of crosslinking in films of poly (butyl methacrylates) is illustrated in Figure 7a using data for poly (n-butyl methacrylate) (Elvacite 2044) and poly (i-butyl methacrylate) (Elvacite 2045). Significant amounts of material insoluble in either toluene or acetone are formed in 884 hours of aging. The amounts are higher for Elvacite 2045, because it has a tertiary carbon atom in the alkyl side group, which has a higher susceptibility to oxidative degradation reactions. Tinuvin 292 at 2% slows the crosslinking process, although not to an extent that warrants recommending its incorporation in poly (butyl methacrylate) coatings.

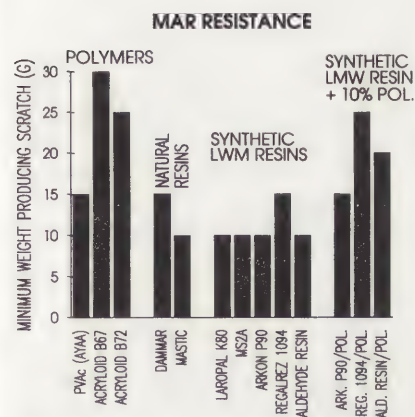
Figure 7b shows comparable data for LMW resin/polymer mixtures. After 2269 hours of aging, the Arkon P90/Kraton G1652 combination shows significant development of material insoluble in cyclohexane or toluene, but it remains largely soluble in acetone, illustrating that no insolubility due to crosslinking occurs. Addition of 2% Tinuvin 292 slows the degradation process considerably. The Regalrez 1094/Kraton G1652 combination shows remarkable stability, even without the addition of Tinuvin 292, as does the aldehyde resin/Elvacite 2044 combination. Films of other HHC resin/Kraton G series mixtures show similar results. Crosslinking apparently does not play a role in the solubility of these LMW resin/polymer combinations.

FTIR

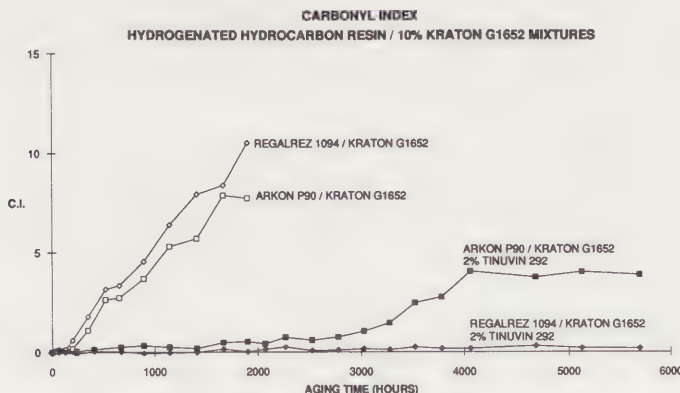
Figure 8 shows the carbonyl index during aging for almost 6000 hours for HHC resin/Kraton G1652 combinations. A considerable change can be seen for the



9. 60° gloss of polymeric varnishes, natural resin varnishes, synthetic low-molecular-weight (LMW) varnishes, and varnishes containing mixtures of LMW resins and polymers, applied over a rough paint surface. The polymer mixed with Arkon P90 and Regalrez 1094 was Kraton G1650. Elvacite 2044 was mixed with the aldehyde resin. Polymer concentrations in the mixtures were 5% and 10%.



10. Mar resistance of films of polymers, natural resins, synthetic low-molecular-weight (LMW) resins, and synthetic LMW resin/polymer mixtures. The polymer mixed with Arkon P90 and Regalrez 1094 was Kraton G1650. Elvacite 2044 was mixed with the aldehyde resin. The polymer concentration in the mixtures was 10%.



8. Carbonyl index of films of unstabilized and stabilized hydrogenated hydrocarbon resin/Kraton rubber mixtures during aging in a xenon arc Weather-ometer.

unstabilized films, while the effect of stabilization is evident for both resin combinations.

Gloss and mar resistance

To learn how these polymeric additives may affect the working properties of varnishes and the appearance achieved with them, varnishes were applied over roughened paint surfaces. Varnishes cause an increase in gloss and color saturation by leveling microscopically rough surfaces [3]. Figure 9 shows the results of 60° gloss measurement of these samples. Although there is a considerable component of experimental variance, in that the surfaces obtained depend on application, the graph illustrates that natural resins and LMW synthetic resins have the ability to produce high gloss, that polymers give much lower gloss and that the LMW resin/polymer combinations allow for considerable reduction of the gloss. Further optical characterization of varnished paint samples, including color measurements, is underway.

To determine the effect of polymer additives on the brittleness of coatings, the mar resistance was determined using a balanced-beam scrape-adhesion and mar tester. Although this test gives crude data, the results in Figure 10 show that the mar resistance of films of natural and synthetic LMW resins is lower than that of polymeric films and that the mar resistance of films of LMW resin/polymer combinations is increased. More sophisticated mechanical tests on these varnishes are underway.

Conclusions

Films of the hydrogenated hydrocarbon resins Regalrez 1094 and Arkon P90 and an experimental aldehyde resin resist aging in a xenon arc Weather-ometer, in which daylight through window glass (including the UV component) is simulated, to a much greater extent than films of the ketone resin Laropal K80 or the reduced ketone resin MS2A. Of these three synthetic low-molecular-weight resins, Regalrez 1094 and the aldehyde resin are the more stable. In order to obtain long-term stability, the hindered amine light stabilizer Tinuvin 292 should always be added to these resins at 2%. Films of hydrogenated hydrocarbon resins containing 10% of any of the Kraton G series rubbers in Table I and 2% Tinuvin 292 as well as films of the aldehyde resin containing 10% Elvacite 2044 and 2% Tinuvin 292 are also very stable. Insolubility caused by crosslinking does not appear to occur in films of these low-molecular-weight resin/polymer mixtures.

Elvacite 2044 appears to be a good additive for the aldehyde resin. Kraton G series rubbers, particularly Kraton G1650 and G1657, appear to be good polymeric additives for Arkon P90 and Regalrez 1094 varnishes. The lower-molecular-weight rubbers, Kraton G1652 and G1726, may not modify solution and film properties substantially. The high-molecular-weight Kraton G1750 (hydrogenated polyisoprene) may be a useful additive for some applications but it gives solutions of relatively high viscosity. Although the full benefits of addition of these polymers remain to be determined, brittleness of varnish films may be reduced and handling properties of solutions improved. By adding

different amounts of polymer, coatings can be tailored to specific needs. This study was limited, however, to polymer concentrations of 10% and at higher concentrations aging behavior may differ.

Experimental

Accelerated aging

An Atlas Ci65A xenon arc Weather-ometer with a borosilicate inner and soda lime outer filter glass was used. This filter combination cuts off short-wavelength ultraviolet radiation and provides a simulation of daylight through window glass. The xenon arc output was controlled at 420 nm and was maintained at an irradiance of 0.90 W/m². Other settings were: black panel temperature 50° C, dry bulb 35° C and wet bulb depression 10° C. No other UV-absorbing filters were used during these experiments.

Removability tests

Solvent mixtures of increasing polarity were gently dabbed onto the resin film surface using cotton swabs, while observing the surface under a stereo microscope. The procedure has been described in detail in a previous paper [12].

Tests for insoluble material

0.5–2 mg of the resin film were scraped from the glass plate, weighed and placed in a 400 mesh stainless steel wire basket of ca. 25 × 20 × 12 mm, which was then weighed. The basket was placed in a covered glass beaker containing about five ml of the appropriate solvent and placed on an orbital stirrer for one hour. The basket was then taken out of the solvent, allowed to dry for one hour at room temperature and weighed. The percentage of resin left in the basket was calculated.

FTIR

FTIR spectra were obtained using a Bio-Rad FTS 60-A Fourier-transform infrared spectrometer and a fixed angle (30°) specular reflection accessory of resin films applied on reflecting plates (Mirrored Micro Mounts; Spectra-Tech). Instrument settings were: resolution 8 cm⁻¹, number of scans per spectrum 16, scan speed 5 kHz. Film thicknesses were determined by white light interference spectrometry, using the Zeiss MCS330 multi-channel diode array spectrometer, CLX111 xenon lamp, fiber optics and SDickm film thickness measuring program.

Gloss measurements

Rapidly drying polyurethane paint was spread on aluminum panels to give hard, inert surfaces. The smooth and glossy surfaces were abraded using nylon pads to introduce some surface roughness and a matte appearance. One varnish layer was applied by brush over the matte surfaces. Extensive brushing was used, as is common practice during the application of natural resin varnishes. Subsequently, a spray coat was applied. Gloss values were determined using a BYK-Gardner micro-TRI-gloss apparatus.

Mar resistance

Mar resistance was determined using a BYK-Gardner Balanced-Beam Scrape-Adhesion and Mar Tester, according to ASTM method D2197. The instrument employs a 45° stylus which was drawn over the surface of the film under varying loads. Loads were increased in 5g increments until the first perceptible scratch was formed.

Acknowledgments

Michael Beverly, Stephen Funk and Michael Palmer prepared samples for accelerated aging, carried out solubility tests and measured infrared spectra. Suzanne Lomax developed the test for insoluble material. Tom Learner prepared samples, and performed gloss measurements and mar resistance tests. BASF kindly supplied the aldehyde resin. Valuable comments to the manuscript were made by Barbara Berrie, Sarah Bertalan and Christopher

Maines. The author is grateful to the National Gallery of Art and the Mellon Foundation for making this work possible.

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12. E. R. de la Rie, "Photochemical and Thermal Degradation of Films of Dammar Resin," *Studies in Conservation* 33 (1988): 53-70.

Suppliers of resins and additives

ARAKAWA CHEMICAL (Arkon P90):

1-3-7, Hiranomachi, Chuo-ku 541, Japan, tel 06-209-8580, fax 06-209-8542.
615 N. Michigan Ave., Suite 1700, Chicago, IL 60611, USA, tel 312-642-1750, fax 312-642-0089.
Kajen 2, 2000 Hamburg 11, Germany, tel 040-364275, fax 040-362839.

HERCULES, RESINS GROUP (Regalrez 1094):

Hercules Plaza, Wilmington, DE 19894, USA, tel 800-247-4372, fax 302-594-5471.
Veraartlaan 8, 2288 GM Rijswijk, the Netherlands, tel 703-150000, fax 703-150356

BASF CORP. (Aldehyde Resin), not commercially available.

CIBA-GEIGY, ADDITIVES DIVISION (Tinuvin 292):

Seven Skyline Drive, Hawthorne, New York 10532-2188, USA, tel 800-431-1900, fax 914-479-2779.
Postfach, CH-4002 Basel, Switzerland, tel 061-697-1111, fax 061-697-7444.

SHELL (Kraton Rubbers):

3200 Southwest Freeway, Suite 1230, Houston, Texas 77027, USA, tel 800-457-2866, fax 713-241-8107.
Postbus 2960, 3000 CZ Rotterdam, the Netherlands, tel 010-469-6915, fax 010-469-7088.
Heronbridge House, Chester Business Park, Wrexham Rd, Chester CH4 9QA, United Kingdom, tel 0244-685-000, fax 0244-685-010.

DU PONT (Elvacite 2044):

Wilmington, DE 19898, USA, tel 800-458-2483, fax 302-773-2706.
Charles Tennant Co., Denney Ave, Waltham Abby, Essex, EN9 1NS, United Kingdom, tel 0992-715777, fax 0992-70049.
Sepulchre, S.A., 19-B6 Ave de Nenuphars, B-1160 Brussels, tel 02-672-2335, fax 02-673-6782.

Abstract

In paintings on canvas, there are portions where hardening of oil colors is greatly delayed. This may be a serious hindrance in the production of paintings. The delay always occurs in portions of the canvas where the stretcher is located. The effect of wood used in stretchers on the delay of hardening of oil colors has been investigated.

A "compression spread" method was developed to measure objectively and accurately the degree of hardening of oil colors. In this method, the degree of hardening of oil color can be measured from the spread-area-ratio.

Extractives from western red cedar (*Thuja plicata* D. Don), were added to the oil colors in small amounts and the degree of hardening was measured. Compared with untreated oil colors, it was found that those with added extractives required three times longer to harden. It is clear that the delay in hardening is caused by these extractives. When the wood is put in contact with canvas for an extended period, the extractives transfer into the canvas and the delay of hardening of oil colors takes place in the affected regions.

Keywords

Extractive, oil color hardening, canvas, wood stretcher, western red cedar

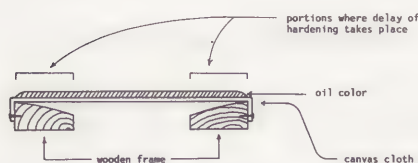


Fig. 1 Oil painting canvas

Retardation of Oil Color Hardening by Extractives from Wooden Canvas Stretcher

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Introduction

In paintings with frames of western red cedar, there are portions of the canvas where the hardening of oil colors is greatly delayed. This is a serious problem in the production of paintings and similarly, a serious hindrance in their preservation.

Because all the hardening delay phenomena appear in portions of the surface where the wooden stretcher is in contact with the canvas (Fig. 1), it can be assumed that the wooden stretcher is responsible. For the paintings in question, the canvas is attached to the stretcher with nails to give a moderate tension. The tension should be sufficient to prevent slacking off from the stretcher due to the change in temperature and/or relative humidity. In Japan, western red cedar (*Thuja plicata* D. Don) is now most widely used for wood stretchers. In these experiments, the effect of western red cedar wood stretcher on the delay of hardening of oil colors has been investigated.

Measurement of the degree of hardening of oil colors

There has been no method for measuring the degree of hardening of oil colors. Hardening has been judged objectively by touching with a finger. Thus the compression-spread test was developed.

Circular test specimens (15 mm diameter, 0.7 mm thickness) of oil colors (permanent white and chinese red, Holbein Co.) were spread on the surface of canvas (50 mm × 50 mm). The test specimens were then dried within a temperature and relative humidity-controlled room (temperature = 25 °C, RH = 55 %). After each day, 3 test specimens were taken out and a polycarbonate board (100 mm × 100 mm) was carefully placed on top of the oil color circle for 1 minute. The difference between the area after removing the board and the initial area was taken as the spread area (Fig. 2).

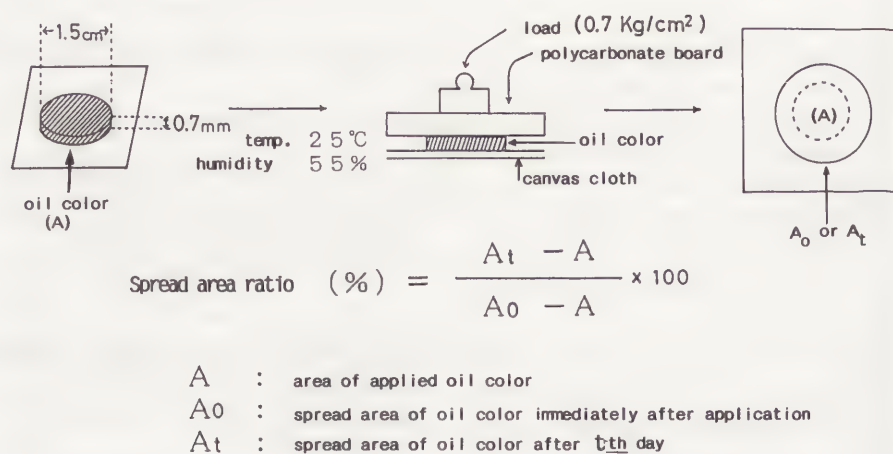


Fig. 2 Method of measuring the degree of hardening of oil color

For each measurement during the hardening period, the average spread area was determined for the three test specimens. This average was divided by the area

* Author to whom correspondence should be addressed.

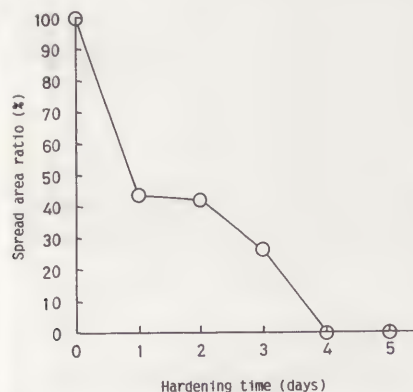


Fig. 3 An example of the measurement of the degree of hardening of oil color (spread area ratio) by compression spread method

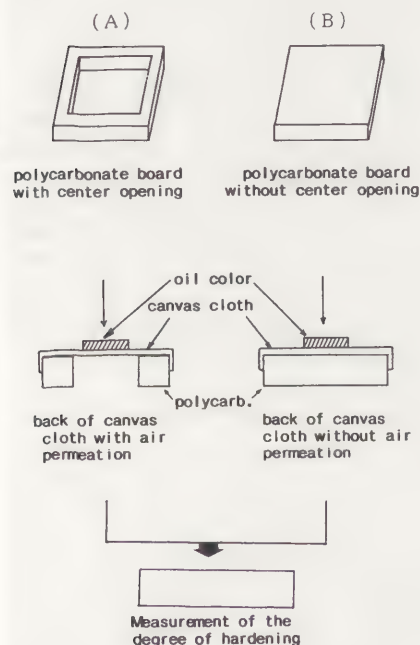


Fig. 4 Scheme of test for the effect of air permeation on hardening of oil color

at zero time (i.e. the area just after the application of the oil color). The ratio is presented as a percentage. If the area of oil color which adhered to the polycarbonate board became smaller than the initial area, it was given a value of zero. The time at which adhesion of the oil color to the board ceased was taken as the hardening time.

An example of the results with the above is shown in Fig. 3. More accurate measurement of the extent of hardening with time compared with finger touch judgment has been made possible.

Cause of the delay of hardening of oil colors

Investigation of the effect of air and the accessibility of air to the back of the canvas

The delay of hardening of oil colors was observed only in areas of the canvas covering the stretcher. Therefore, an investigation of the effect of the stretcher on the delay of hardening was conducted. First, the effect of the frame as an obstruction reducing the access of air to the canvas was studied.

Experiment

As shown in Fig. 4., the center of a polycarbonate board (80 × 80 mm) was cut to make an opening (60 × 60 mm). Boards without this opening were also prepared. Canvas samples were placed and fixed on top of both boards with a pair of clips. At the center of the canvas, oil color was applied and the hardening measurement test was conducted. Comparison was made of the hardening process on both types of board. The commercial oil colors (Holbein Manuf. Co.) tested were chinese red, a slow hardening color and permanent white, a fast hardening color.

Results and Discussion

The hardening process expressed as the change in the spread area percentage is shown in Fig. 5. According to the results, the colors on boards with or without

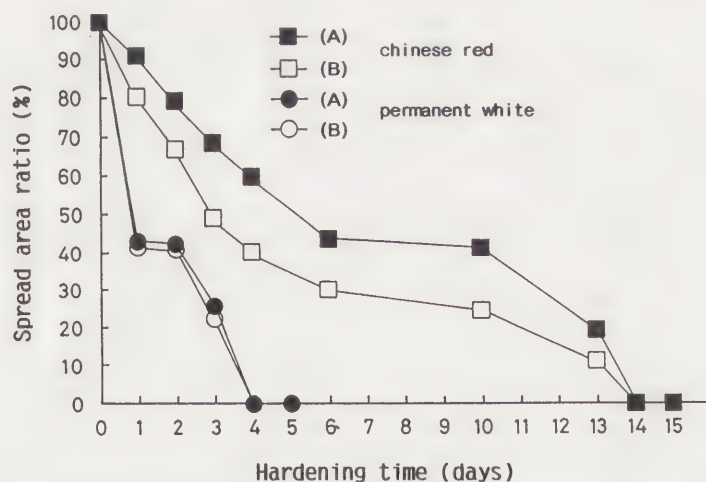


Fig. 5 Effect of air permeability of the back of canvas cloth on hardening of oil colors
(A): polycarbonate boards with center opening
(B): polycarbonate boards without center opening

the opening at the center showed almost the same hardening rate and consequently the same time (total number of days) to complete hardening. At the early stage during the course of hardening of chinese red, there was a small difference between boards with and without the central opening. Colors on unopened boards (obstructed air access) showed faster hardening compared to those with good air accessibility. For permanent white, very similar hardening rates and hardening times were observed. Chinese red hardened taking 3 times longer to harden (15 days) than permanent white.

From the results, it was ascertained that measuring the degree of hardening

using the spread-area-percentage, was highly accurate. Also, it was verified that the delay in hardening of oil colors caused by canvas stretchers does not arise because of reduced air access.

Effects of western red cedar extractives

Since the delay in hardening of oil colors is not caused by the reduction of air access, it was speculated that there is something in the wood which causes the delay, thus, the effect of the extractives was investigated.

Experiment

Wood meal (40–60 mesh) of western red cedar (as used in a frame) was Soxhlet extracted with ethanol-benzene (1:1) for 6 hours. The solvent was evaporated and the dried extractives were ground into a fine powder. The powder was then mixed thoroughly into the oil paint at 0.1% (by weight) until dissolved. The oil colors with added extractives and without extractives were applied directly to the polycarbonate boards and the degree of hardening was measured. Permanent white was used in the test.

Results and Discussion

The drying process of oil color with and without extractives is compared in Fig 6. The hardening time of oil color plus extractives was 17 days, while oil colors

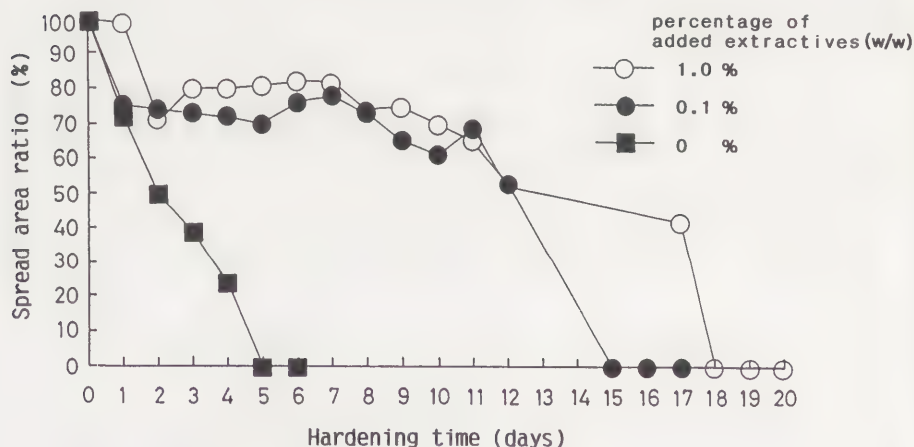


Fig. 6 Effect of extractives on the hardening of oil color

without extractives hardened in 6 days. However, there is almost no difference between the hardening times of color with 0.1% extractives (17 days) and 1.0% extractives added (20 days). Up to the 13th day, there was almost no difference in the rates of reduction in spread area between the oil colors with differing percentage extractives. These results revealed that the extractives of western red cedar contain components which can impede the hardening of oil colors even at microscopic quantities.

The main ingredients of permanent white oil paint are titanium dioxide and poppy oil. Hardening involves curing of the oil by oxidation. The portions which do not cure adhere to the polycarbonate board placed on top of the oil color and spread. As curing proceeds through oxidation, the spread area decreases.

It was reported that the extractives of western red cedar are phenol compounds as well as other aromatic compounds (tropolones) (1,2,3). These extractives contain compounds which inhibit oxidation reactions similar to the way in which antioxidants function. Hence, it was realized that extractives have antioxidant effects which limit the oxidative curing of oil colors, thus causing the delay in hardening.

Transfer of extractives into canvas cloth from the stretcher

It is not yet clear how the extractives transfer into the canvas cloth. Two possibilities have been considered and experiments were conducted to elucidate them.

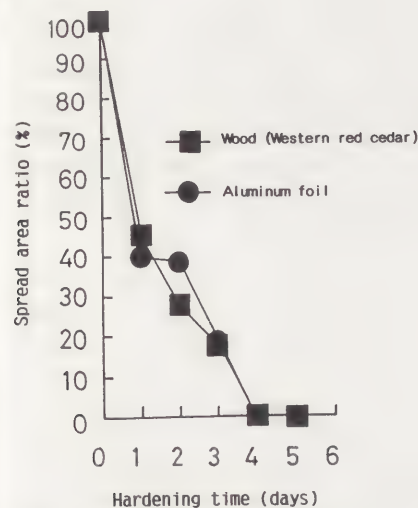


Fig. 7 Comparison of the degree of hardening of oil color on canvas cloth attached from the back to the wood or aluminum foil

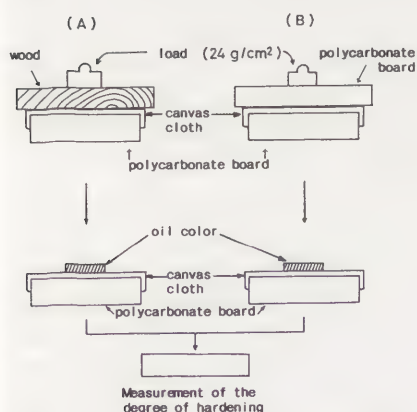


Fig. 8 Scheme of test for comparing the degree of hardening of oil color on canvas cloth previously in contact with wood or polycarbonate board for extended period of time

Transfer from the back of the canvas

Since the stretcher is in direct contact with the canvas, it was thought that extractives migrate from the back of the canvas towards the canvas surface. This was investigated with the following experiment.

Experiment

Western red cedar boards were prepared with stretched canvas in direct contact and with aluminum foil between the canvas and the wood surface. The boards without aluminum foil allow the extractives to move from the back to the canvas surface while the covered boards were designed to prevent such movement. Oil color (permanent white) was applied by the same method as above and the degree of hardening measured.

Results and Discussion

As shown in Fig. 7, the hardening rates for oils applied to canvas placed on covered and uncovered wood boards were almost the same. Complete hardening occurred after 5 days on both specimens. Thus, the results do not support the hypothesis that extractives from the wood which is in contact with the back of the canvas penetrate and also exude from the surface of the canvas.

Direct movement into the canvas cloth

If the movement is not from the back of the canvas, it suggests that the extractives transfer into the canvas surface by direct contact between the wood and the canvas. It is thought that this is caused during the manufacture and storage of stretched canvases. In storage, stretched canvases are piled up so that the wood used in one stretcher is placed directly on the surface of another canvas below, and under considerable pressure. It seems likely that the wood extractives move into the surface of the canvas in this storage period.

Experiment

As shown in Fig. 8, a western red cedar board was placed on the surface of the canvas mounted on the polycarbonate board under tension. On separate specimens, the polycarbonate board replaced the wood. A load exerting a pressure of about 24 g/cm² (the approximate pressure in a pile of 30 framed canvases during storage) was placed on top. The specimens were left thus for one week. The wood (or polycarbonate) boards were removed and immediately, oil color was applied on the surface of the canvas. The degree of hardening was measured and compared.

Results and Discussion

Fig. 9 shows the hardening process of oil colors applied to canvas upon which wood or polycarbonate boards had been placed. It took only 6 days for the color

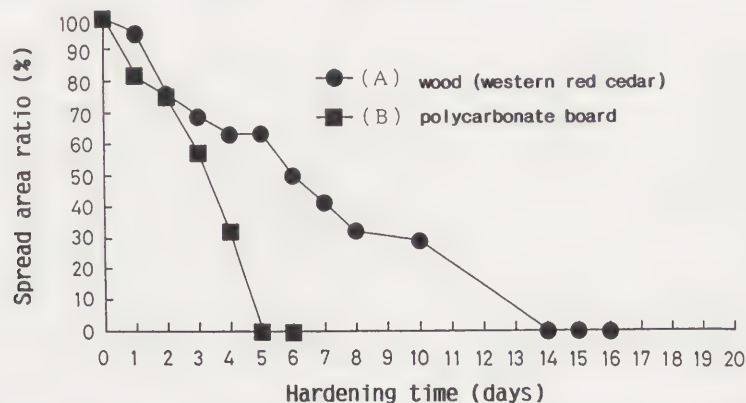


Fig. 9 Effect of long time contact between canvas cloth and wood or polycarbonate board on the degree of hardening of oil color

to harden on canvas which was previously in contact with polycarbonate board, a period similar to that of the previous experiment. Contrary to this, the rate

of hardening of oil canvas which had been in contact with wood was greatly delayed and took about 16 days to complete the process. This time is similar to the hardening time of colors with 0.1% extractives added as described in the previous experiment. From the results, it was deduced that by placing the wood in contact with the canvas for an extended period, the extractives which delay hardening of oil colors transfer into the surface. Consequently, it was ascertained that the hardening delay occurs in parts of the canvas where wood has been in direct contact while canvases are stacked in storage.

The extractives studied consist mainly of the involatile portion. This is so because in the Soxhlet extraction method, the solvent had to be evaporated at temperatures as high as 60°C. At these temperatures, most of the volatile compounds should have evaporated. The presence of a small fraction of volatile extracts in the volatile residue is confirmed by the "sweet/aromatic odor", which also indicates the presence of components with intermediate volatility. The latter are involatile enough not to be removed at 60°C but volatile enough to be detected by their odor. Though it is not yet certain, these compounds of intermediate volatility are the likely cause of the problems based on the fact that they are not so volatile as to diffuse quickly towards the surface and escape into the atmosphere and not so involatile as to remain inside the wood. These intermediately volatile extracts slowly diffuse towards the surface and remain there longer.

It seemed to us that the volatile components would not remain in canvas long enough to influence the rate of drying. From the time of mounting the canvas into the stretcher, to stacking them up, and then to actual painting, most of the volatile extracts might have escaped into the atmosphere. Because these components of the extracts with higher molecular weights take longer to diffuse (i.e. they have limited mobility) into the canvas, it follows that they tend to stay there longer.

Up to the present, there have been no cases where a hardening delay has occurred in all areas on the surface of the canvas where the wood stretcher has been in contact. Therefore, there is a need to elucidate the conditions involved in the movement of a particular extractive into the canvas. For example, factors such as whether the wood is heartwood or sapwood, contact pressure and the environmental conditions should be considered. Moreover, because the extractives retard the hardening of colors, a study which deals with the influence of extractives on the preservation of paintings should be conducted for the next stage of the research.

The main thrust of the present and future experimental work focuses on determining the particular components responsible for the delay of drying.

Conclusion

The conclusions may be summarized as follows:

- A new method (the compression spread method) for measuring the degree of hardening of oil colors has been developed. Through the measurement of spread area ratio, the method can be used to investigate the drying process and the degree of hardening of oil colors objectively.
- The delay in hardening of oil colors is not caused by a reduction in the access by air to the back of the canvas caused by the presence of the wood stretcher. It was proved that the extractives of western red cedar greatly retard and consequently delay the hardening of oil color. This phenomenon occurs even when the extractives were added to the color at very low 0.1% (by weight) concentration. Drying rates for colors with extractives added at either 0.1% or 1.0% by weight are almost the same.
- The effect of the extractives from the wood stretcher does not result from the transfer from the back of the canvas. It was made clear that the effect was brought about when the stretchers are in direct contact with the surface of the canvas for an extended period of time while stacked in storage. The extent of the delay brought about is similar to that when oil color has 0.1% wood extractives added.

From the above results, it is clear that the retardation in hardening of oil colors is brought about when the western red cedar is in contact with the surface of the canvas for extended periods. It was proved that the wood extractives transfer to the surface of the canvas and inhibit oxidation reactions within the oil color and delay hardening.

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Abstract

Few of the resins used to conserve objects were developed specifically for that purpose. For that reason, the British Museum has a policy of assessing all materials prior to their use with objects. Procedures for determining the tensile properties of resin films and adhesive bonds were defined in the early 1980s, but it is now felt that a more extensive repertoire of mechanical tests is necessary with the increase in the range of available formulations and conservation techniques. This paper describes the development of the standard tests for testing materials currently used by the Conservation Research Section of the British Museum, their applications and limitations.

Keywords

Mechanical testing, materials, resins, testing, standard tests

Mechanical Testing of Resins for Use in Conservation

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Introduction

Conservators use a wide range of resins in the form of consolidants, adhesives, decorative, and protective coatings. However, few of these materials are intended for use in conservation and are formulated for either industrial or household applications. It is the policy of the Department of Conservation that all materials to be used in contact with museum objects should be assessed for their stability with regard to, at least, the next fifty years.

In the early 1980s, research into the methods of ageing resins and assessing their stability was carried out by Bradley in the British Museum (1). Since that time, the repertoire of tests has expanded in order to include new equipment and the more varied requirements of conservators. It was felt necessary to develop a set of standard tests that defined the procedures used in the British Museum for the evaluation of resins.

In the United Kingdom, industry mostly uses British Standards Institute test procedures, although specifications relating to the American Society for Testing and Materials (ASTM) and other bodies are in use; many non-standard tests are also quoted. Such a diversity of procedures reduces the ability to compare results from different sources. In addition, the lack of a set of test procedures accepted by all museum professionals has led to repeated testing of the same material by different institutions. Since there was little value in "reinventing the wheel," the standard tests defined by the author were based on British Standard tests, but were adapted to take into account the requirements of conservation rather than industrial materials, and the equipment available in the Conservation Research Laboratory.

The purpose of this paper is to describe the development of the standard tests, their applications and limitations. The measurement of shrinkage, hardness, bond strengths and adhesion of resins is discussed. Since the standard tests are lengthy, the only ones included in the text are those describing the bonding strengths of adhesives to ceramics and the pencil hardness test.

Preparation of samples for testing

The mechanical properties of resins are most readily studied when in the form of coherent, cured free films. This minimises any effects due to the flow of the polymer solution and represents the form in which the resin will be present on an object. In order to produce a material which may be readily handled, it is necessary to cast thicker films than those applied to objects. Non-drying resins, such as butyl methacrylate dispersions, are cast onto glass microscope slides for ease of handling and are evaluated on glass.

Recently, the palette knives formerly used to spread resins were replaced with wirewound bar coaters; the latter are used in the surface coatings industry to produce films of a known wet film thickness (2). Coaters comprise a steel rod onto which a length of wire of known diameter has been wound. When drawn through the solution to be cast, resin collects in the grooves between adjacent sections of wire and is redeposited on a sheet of polythene which has been taped around a flat glass plate. The thickness of the resulting wet film depends on the viscosity and hence the flow of the resin solution. A 50-micron coater is most commonly used in the British Museum.

If thicker films are required, further films may be cast over the original layer when it has cured. Cured films are then peeled from their polythene backing. Measurements by permascope, an instrument that measures the current induced

between a probe and an aluminium plate placed beneath the free film, have shown that the use of a wirewound bar coater produces significantly more films of even thickness than was achieved with a palette knife.

Accelerated ageing

In a paper presented at a previous ICOM conference, Feller stated that "the basic objective (in choosing materials suitable for use in conservation) is to select materials that could be expected to suffer a loss of no more than 20% of their essential properties in 100 years' exposure under normal museum conditions" (3). Since we do not have the luxury of time, the ageing process needs to be accelerated so that any changes in the properties of a material may be detected within a reasonable time span. This is achieved in practice by increasing the energy of the system using heat and light in order to speed any reactions which may occur with time.

Table I. Comparison of effect of ageing cellulose nitrate film at various temperatures, calculated using the Arrhenius equation.*

Ageing temperature (T°C)	Equivalent ageing periods at T°C for denitration of cellulose nitrate (years)
20	1
30	4.3
60	194.4
70	601.8
100	12292.1

$$* \log \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where

k_1 = the rate constant at 20° C, T_1 (in degrees Kelvin),

k_2 = the rate constant at a higher temperature, T_2 (in degrees Kelvin),

E_a = the Activation Energy for cellulose nitrate (107kJ/mole) (9),

R = the Universal Gas Constant.

In addition to accelerating reactions that take place at room temperature, mechanisms occur which are only initiated at high temperatures. Thus, they obscure the true behaviour of the material. Different heat ageing regimes are in use in various institutions: the most commonly used temperatures are 70°C and 100°C. Calculations made using the Arrhenius equation suggest that ageing at 70°C represents better the required useful lifetime (50 years) of a material than ageing at higher temperatures for the same period of time (See table I). In the British Museum, films are heat aged in stoppered Quickfit tubes in a convection oven at 70±1°C and examined weekly for changes in any properties appropriate for their intended use. However, the suitability of this regime is dependent on the material. A recent study into the properties of cellulose nitrate adhesive showed that ageing at 70°C had predicted a greater level of deterioration than was observed in practice (4). In addition, the problems of ageing thermoplastic resins above their Glass Transition temperatures (T_g) must be considered. Current practice is to heat age these materials, which include some of the most stable and widely used acrylics in conservation, below their T_g until some change is detected.

The purpose of light ageing is to reproduce the behaviour of a material which is exposed to daylight once it has been applied to the objects (mostly consolidants and fillers). Objects on display in artificially illuminated galleries of the British Museum are exposed to UV-filtered light for an average of 44 hours each week.

At present, a Microscal light fastness tester fitted with a 500-watt phosphor-coated bulb is used to light age free films of resin in this laboratory. The lamp provides a similar distribution of wavelengths to daylight, but at approximately 200 times greater intensity. Since the energy output of the bulb changes with time, due to loss of the phosphor coating, blue wool standards are used to quantify the period of ageing. At a recent meeting of conservation scientists in the United Kingdom, it was agreed that a standard light box should be developed to replace the Microscal tester, using fluorescent tubes and UV filters in order to better replicate the conditions prevalent in a museum showcase.

There is little doubt that natural ageing is preferable to accelerated deterioration. Free films of all materials assessed, aged and unaged, are kept in the dark under reasonably constant temperature and relative humidity. Samples are kept in the dark mainly due to constraints on storage space. The storage of these films has resulted in a reference collection of resin films of all types dating back 20 years; such samples have proved useful when comparing artificial and natural ageing regimes.

Shrinkage

Linear shrinkage may be caused by the removal of solvent from a drying film or by a change in the density or orientation of polymer molecules. It is important to be aware of the magnitude of shrinkage before applying a resin to an object, since it indicates the magnitude of forces set up when the resin is applied to a surface. Early techniques for determining the shrinkage of resins that cure by solvent evaporation alone involved casting a thin film of resin in a plywood

frame and examining the extent of distortion on drying. The results of this method gave a good indication of the way in which the resin interacted with absorbent substrates, but they were less transferable to non-absorbent substrates.

Since there is no British Standard test specified for shrinkage of flexible polymers, a simple test was developed. A flat glass plate was covered with polythene sheeting; four crosses, each at the corner of a 20 mm square, were marked on the surface using a fine-tipped ballpoint pen. The distances between the centres of the crosses were measured using calipers. A film of the test resin was cast on the polythene using a 50-micron wirewound bar coater. When dry, the film was peeled from the plate, and the distances between the crosses, which had transferred from the polythene, were remeasured. The mean percentage shrinkage was calculated.

The shrinkage of resins that cure by cross linking, such as epoxies, may be determined by pouring the pre-mixed material into a greased, stainless steel die. Once cured and released, the resin block is measured daily using a micrometer screw gauge, and the mean shrinkage is calculated. This method has been used at the British Museum since the late 1960s (1).

Hardness

"Hardness" is not a fundamental property, hence the definition of the term is often subject to discussion and confused with similar terms, such as "brittleness," stiffness," and "toughness." "Hardness" is used in this paper to describe the resistance of a material to indentation. Recent British Standard procedures such as BS2782 Part 3 Method 365A define softness (the inverse of hardness) as the depth of indentation of a steel ball of set diameter and known weight after application to the test piece for 30 seconds (5). Resins applied to the surfaces of objects must be resistant to the forces associated with day-to-day handling and packing. Since the British Standard test involves the use of specialised apparatus not available in the museum and does not represent the most likely force imposed on consolidants, a simpler "low-tech" method from the surface coatings industry was adopted.

The aim for this standard test is to determine the hardness of a cured surface coating. The theory involved in the test is the measurement of the resistance of a film to the impact of a pencil point. The necessary apparatus and supplies include a set of Venus drawing pencils (6B-9H), P280A fine silicon carbide paper, a pencil sharpener, and a glass plate approximately 0.5 cm thick. The materials required include the sample to be evaluated. The procedure for the test is as follows:

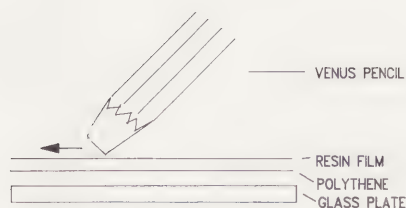


Figure 1. Pencil hardness test.

1. Cast a film of the sample on the glass plate to the required thickness. Allow to cure or dry thoroughly.
2. Sharpen the pencils and flatten the points by making circular movements on the silicon carbide paper.
3. Holding the softest pencil at a 45° angle to the film, push the lead firmly across the surface (see fig. 1). Repeat with harder pencils until one is found that will just indent the film.
4. Repeat procedures in two other areas of the film.
5. Measure thickness of cured film (by travelling microscope or permascope).
6. Measure the temperature and relative humidity at the time of the test.

Results of hardness test

The hardness of the film is described as the hardness of the pencil which just indents the film under the prevailing conditions of temperature and relative humidity.

The test is simple to perform and interpret, and has the benefit of accessible, low cost equipment. However, the result obtained depends upon the pressure exerted on the pencil and on the quality of pencil used. It is intended to reduce the variability of pressure by loading the pencil, based on published findings (6). Such adjustments would improve the reproducibility of the procedure.

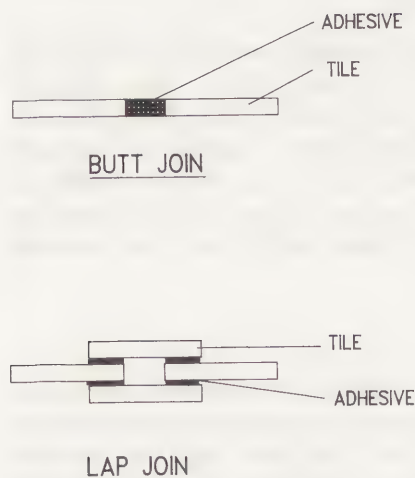


Figure 2. Test pieces for tensile testing of adhesive bonds.

Tensile testing of adhesive bonds

Repairs to objects either involve adhesion of two broken edges or overlaying the loose piece with the main body. Two factors may be used to establish the strength of adhesive bonds on rigid substrates: their resistance to shear and tensile forces. In practice, a bond may be subjected to tension and shear forces simultaneously, so that the measurements are used as a means of comparing the adhesive power of several materials under repeatable, controlled conditions.

The following standard test describes theory and practice in the case of adhesives for ceramics. The aim is to determine the breaking stresses of bonds made between adhesives and ceramic substrates. In theory, this test measures the breaking stresses of two types of bond. The butt joint is the most common type of repair made in conservation and is used for attaching two pieces of the same cross-sectional area. Lap joints are formed when the adhesives overlap, e.g., during the laying of paint flakes. A stress is applied until the test joints fail at the interface between adhesive and ceramic. The apparatus required includes a J.J. Lloyd Tensile Testing Machine T 5003 and a tile cutter. The materials required include the adhesive for evaluation and ceramic tile pieces. The procedure for the test is as follows:

1. Preparation of test pieces

- (i) Cut pieces of ceramic tile 2×5.5 cm, two for each butt joint and four for each double lap joint. Abrade one of the shortest edges to smoothness using silicon carbide paper, ensuring that the edge is perpendicular to the body of the tile.
- (ii) Apply a thin layer of adhesive to both halves of a butt joint and to the four positions indicated for a double-lap assemble joint (See fig. 2). Allow to dry for at least 48 hours on a flat surface prior to testing.
- (iii) Condition test pieces at $65 \pm 5\%$ relative humidity and $20 \pm 2^\circ\text{C}$ for two hours prior to testing.

2. Tensile testing

- (i) Fit suitable load cells for the adhesive (50 N for butt joints prepared with cellulose nitrate and 500 N for lap joints prepared with cellulose nitrate or Paraloid B72). Attach the serrated grips to the fixed and moving edges of the cross-head.
- (ii) Clamp the joint between the grips, adjusting the distance between them, so that the grips are equidistant from the centre of the repair, using the cross-head control buttons and "up" and "down" switch.
- (iii) Set the load cell and cross-head to zero.
- (iv) Select the speed required (500 mm/min is suitable for cellulose nitrate and Paraloid B72).
- (v) Select the required paper/cross-head ratio and the sensitivity.
- (vi) Set up the chart recorder, zeroing the pen and calibrating it using the push buttons labelled "strain" and "stress" on the body of the machine, and the sensitivity knobs on the chart recorder.
- (vii) When ready, set the machine to "up" and press the "start" button. Stop the cross-head when the joint has broken. Discount any test pieces which break in any position other than at the joint. At least ten results are required for each adhesive.

Results of tensile testing

The results are expressed in Nm^{-2} . The stress required to break the join may be read directly from the chart (vertical axis) and the surface area calculated or measured. The mean value is calculated from the expression:

$$\text{Bond Strength} = \frac{\text{Breaking stress (N)}}{\text{Cross-sectional area of bond (m}^2\text{)}}$$

It is important to test an adhesive with its intended substrate since the porosity of the surface will affect the quality and required viscosity of the adhesive.

Manufacturers of glass adhesives use the test methods defined by ASTM D2095-

69 and BS5350 Part C5:1976 to evaluate their product, both of which refer to the use of lap joins (8). Butt joins are weaker, however; thus, they better represent the problems often faced by glass conservators.

A procedure recently developed at the British Museum uses a 10-cm length of glass rod (6 mm in diameter). The rod is cut midway with a diamond-tipped cutter, and the fresh break is repaired using the adhesive under study. After an appropriate curing period, a rapidly curing epoxy resin is applied with a rough finish, with a spatula, to the last 2 cm at both ends of the rod and allowed to cure. The test piece is tensile tested using serrated grips. The application of epoxy resin to both ends prevents the smooth glass from slipping, thus reducing the number of failures.

Adhesion of resins to a substrate

Pigmented and colourless coatings may be applied to metal, ceramic, glass, and rigid organic surfaces, or to synthetic filling materials for decorative or protective purposes. It is, therefore, important that there is sufficient adhesion between resin and substrate to minimise the penetration of moisture, oxygen, and other corrosive gases. A simple quantitative method of evaluating the adhesion of paint to metal surfaces is described in BS3900 Part E6 (9), and has been adapted to be useful for the measurement of adhesion of consolidants and paint to the surfaces of objects.

The coating is applied to an experimental substrate, representative of that to be treated, and allowed to cure. Using a ruler and fine-bladed scalpel, 11 parallel lines were cut one millimetre apart and approximately 15 millimetres in length so that they penetrated the film but not the substrate. A similar set of lines is cut at right angles to the first; 100 squares are thus produced in total. A piece of Scotch Magic Tape is applied to the grid and pressed onto the surface using an index finger. The tape is pulled briskly (within two seconds) from the surface. The brand of adhesive tape used is important. The concentration and type of backing of adhesive affects the "pulling power" of the tape.

The surface is examined using an optical microscope, and the number of squares either wholly or partially removed is recorded. Since 100 squares have been cut initially, the number damaged or missing is readily expressed as a percentage. Alternatively, a grading from 0 (no damage) to 5 (more than 65% removal) may be assigned as described in BS3900. Since adhesion is dependent on the flow properties of the resin, the relative humidity and temperature at the time of the test should be noted and kept as constant as possible for comparative studies.

Reference materials

It is rarely effective to evaluate materials in isolation; it is necessary either to know the absolute specifications of the resin under test or to compare it with the material currently used. Reference materials are those whose properties are well known and whose measurements are repeatable. Batch to batch variation must be minimal and a range of values known. Testing reference materials alongside experimental resins provides a method to check that the test procedure is being conducted correctly, as well as providing a means by which to compare physical properties. For example, in addition to using Blue Wool Standards to "calibrate" the Microscal Light Fastness Tester, a film of Paraloid B72, a widely used acrylic resin, is aged alongside the test material. Experience in this laboratory has shown that a new 500-watt bulb will induce yellowing of the Paraloid B72 after 2,500 hours. Further work is necessary to obtain a range of suitable reference resins, representative of all the resin types used in conservation. One difficulty with using commercially available formulations is their ability to change without the customer's knowledge.

Conclusion

A set of standard tests has been developed for evaluating the mechanical properties of resins for use in conservation. Most of the standard tests are based on

those defined by the British Standards Institute, but these have not always been used, due to the lack of certain dedicated pieces of equipment. In addition, some of the British Standards tests do not replicate the way a material is used in conservation, which is an important aspect of valid testing procedures. For these reasons, some of the standard tests are tailored to meet the needs of a museum (i.e., the use simple apparatus). Each test comprises a series of simple steps that inexperienced personnel can follow with minimal supervision. Finally, it should be noted that the standard tests will be developed further as new ideas and equipment are introduced to the Conservation Research Section. Ideally, the test procedures could be adapted to form part of a set of museum standards for evaluating conservation materials. This would minimise the quantity of repeat testing carried out by institutions since results would be acceptable to all museum professionals.

Acknowledgements

I would like to thank Susan Bradley and Vincent Daniels for advice on the text of this paper and Andrew Oddy, Keeper of the Department of Conservation, for encouragement to publish.

Suppliers

1. British Standards are available from Sales and Accounts Department, British Standards Institute, Linford Wood, Milton Keynes MK14 6LE, UK. Telephone 0908 326033.
2. Wirewound bar coaters are available from Sheen Instruments Ltd, 8 Waldegrave Road, Teddington, Middlesex, TW11 8LD, England. International Telephone 44 81 977 0051. International Fax 44 81 977 0855.

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Abstract

The feasibility of measuring refractive index (RI) on sub-milligram samples of artists' paint was assessed. Medium-rich paint, glaze and varnish samples are suitable for such testing, and their RI can be measured to ± 0.005 in many cases. New and thermally-aged samples of 19th century oil/resin formulations for gelled media were examined. It was found that there was no increase in RI on ageing, while the presence of lead driers and pigment had a significant effect on the RI of both new and aged material. Modern, unpigmented paint media showed variously increased and decreased RI after thermal ageing. The increased RI expected from the increased transparency of oil paint as it ages was not found consistently in 19th century paintings. Instead, independently analysed glaze samples with high RI were resinous rather than comprising pure oil. The RI of paint seems to depend on its formulation more than on its age. The observed transparency of hundred-year-old paint may be due to complex pigment-medium interactions, some at least involving lead compounds.

Keywords

Refractive index, refractive index measurement, oil paint, oleoresinous paint, resin-based paint, 19th century paint

The Refractive Index of 19th-Century Paint Media: A Preliminary Study

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Introduction

It is well known that oil-based paint grows more transparent with age, and that alterations by the artist, or earlier images, grow more visible with time. Paintings of this century and earlier show this optical effect. It is generally attributed to an increase in the refractive index (RI) of the paint medium, though very few measurements have ever been published. De la Rie quotes earlier work by Feller, in which it is suggested that linseed oil medium may increase in RI from 1.48 to 1.57 (1). This measurement appears to be derived from Laurie's work in the 1930s, where it was found that a linseed oil film increased in RI from 1.480 to 1.515 over 10 years (2). The value of 1.57 refers to the lower layer of a northern Gothic statue of ca 1300, whose priming of "lead white in oil" had an RI of 1.600. This is a very considerable increase, when one considers that some pigments such as ultramarine and chalk have an RI of 1.6: their transparency would increase greatly in such a case (3). Even lead white, with an RI of 1.9–2.1, would look more transparent when immersed in a medium whose RI is 1.57 rather than in fresh oil paint (3). If the RI of the paint medium does not increase significantly, then it must be the RI of the pigment which alters: an idea which is tenable when lead white is involved. (Most pentimenti include lead white.) Lead soaps have been implicated in the drying of oil paint in the industrial paint literature of the earlier 20th century and it is becoming clear from documentary research that interactions between lead pigments and/or driers were postulated in the 19th century as well (4, 5). It may be that lead white does not maintain its identity, at least at the immediate surface of the paint, in dried or aged oil films. (It does in bulk: X-ray diffraction of aged lead white paint is consistent with the results from modern paint.)

The resinous glazes and modified oil media used by many artists in the 19th century have tended to deteriorate badly, darken, shrink and crack, yet they were very popular on account of their desirable handling and optical properties (6–8). Unaltered examples in books of colourmen's samples and the occasional well-preserved painting show a beautiful depth and glossiness. This begs two questions: is the glossiness and pleasing appearance due to the resin having a higher RI than pure oil paint, and thus giving greater transparency to the glaze? Will this optical "advantage" be lost if paint and resin show alterations in RI as they age?

Investigations into the materials and techniques of the artists J.M.W. Turner (1775–1851) and J.A.M. Whistler (1834–1903) provided an opportunity to attempt RI measurement on naturally-aged, 19th century paint, primings and varnishes, and to seek for evidence of increased RI of oil medium. A recent Tate Gallery project on the materials and techniques of artists of the earlier 19th century widened the range of samples available (9). Oleoresinous paint films which had been prepared according to 19th century recipes published in Britain, and some modern gelled paint media, had been submitted to accelerated ageing in an earlier project (10, 11). This gave sufficient thermally-aged material for replicate measurements. Subsequent accelerated ageing projects at the Tate Gallery indicate that thermal ageing, or thermal ageing alternated with exposure to intense, ultraviolet-filtered light, approximate better to natural ageing of oil paint than light ageing alone does, when the end product of ageing is to be used for ultraviolet microscopy and the assessment of microscopic stains (12). Future studies will concentrate on more objective assessments of degradation, by FTIR, for example. "Before ageing" and "after thermal ageing" samples

were utilised for assessing the feasibility and reproducibility of RI measurement by immersion, and for examining the effect of pigment loading and solubility of new or aged samples in RI liquids.

Measurement of refractive index

The measurement of RI by immersing transparent samples in a series of liquids of known RI and observing the increase in transparency until the best-matching liquid is found, is well-known (13). The samples were sub-milligram in mass, 0.1 mm or less in dimension, and were viewed at 40 \times magnification. It was possible to assess whether the sample has a higher or lower RI by observing the movement of the so-called Becke line into the material of lower RI as the microscope is focussed through the sample (14). (The condenser diaphragm of the microscope has to be fully closed to give a prominent border to the sample for focussing and comparing with other samples.) The method is more usually applied to glass, pigments, or geological samples, but any transparent or not too intensely coloured sample may be measured, provided it does not dissolve in the liquids used. Microscopic fragments of glass, a homogeneous material, can be measured to ± 0.003 when RI liquids in steps of 0.01 are used: it is possible to judge whether a sample's RI lies midway between two liquids, or nearer to one of them (15). It is enormously useful for paint samples that the method involves microscopic examination: one can watch samples dissolving, note the inclusion of pigments or other paint or varnish layers, and eliminate problem samples from consideration.

The earlier work by Laurie involved acid dissolution of lead white from white paint samples and RI measurement of the surviving medium (2). His experimental error was ± 0.002 , but the sample preparation may be destructive, especially for new paint films.

A refractometer provides an alternative means of characterising RI. The method is capable of great accuracy on glass samples of 10 \times 20 mm, and of comparable accuracy to the immersion method on glass and liquid samples of 5 \times 8 mm, but is clearly inappropriate for dried paint films and samples from artworks. An inexpensive Dialdex refractometer was used in this study for confirming the RI of the immersion liquids and for measuring the RI of lumps of polished dammar, mastic and copal resins, and drying oils (16). It is useful for the measurement of new and liquid paint and polymer films spread over the prism. The RI of opaque samples can be estimated with a refractometer, but grainy and inhomogeneous samples such as beeswax are impossible to measure.

The RI of materials is weakly dependent on temperature, but the effect is not important at this level of precision. All measurements were at room temperature, 18–20°C.

Table I. RI measurements by immersion on paint media formulated from 19th century recipes. Thermal ageing consisted of 34 days at 70°C and 50% RH in a climate-controlled oven.

Sample	Formula- tion	Before ageing	After ageing
AM1	1:1*	1.497	1.495
AM2	1:2*	1.497	1.497
AM3	1:3*	1.500	1.497
AM4	2:1*	1.495	1.497
AM5	3:1*	1.493	1.500
LM1	1:1†	1.517	1.503
LM2	1:2†	1.517	1.513
LM3	1:3†	1.517	1.513
LM4	2:1†	1.515	1.490
LM5	3:1†	1.517	1.503

* Linseed oil + lead acetate:mastic varnish.

† Linseed oil + litharge:mastic varnish.

RI measurements on 19th-century formulations and modern paint media

The samples consisted of dried paint films on a Melinex substrate. Some were flaked from a priming of Winsor and Newton Foundation White, and some directly from the Melinex. None was immediately soluble in the RI liquids, or showed dissolution in 1–2 minutes.

Two sets of samples (AM1–5 and LM1–5) consisted of linseed oil prepared with two different lead driers, then mixed with mastic varnish in differing proportions, to form a "megilp", a paint medium which gels within a minute of mixing. Repeated measurements of RI on such samples "before ageing" give an idea of the reproducibility of RI measurements by immersion on such samples: no sample showed a major deviation from the rest, and the estimated error on measurement can be taken as ± 0.005 (see Table I).

There was no difficulty in measuring the RI of samples of pure medium, or samples of medium mixed with a modern Van Dyck Brown oil paint from a tube. (Artists of the 19th century mixed "megilps" or other medium modifiers into oil paint on their palette, and then applied the mixture to the canvas—just as would be done with a modern medium modifier.) However, the priming

samples were too heavily pigmented for RI measurement by immersion: the result was closer to the RI of the pigment than to a credible value for the medium; therefore, the method was limited to medium-rich samples.

The period of thermal ageing, although sufficient to produce changes in auto-fluorescence and in the response to fluorochrome staining in several modern paint formulations, did not lead to an increase in the RI of these oleoresinous paint media (12). In fact, the RI of the aged medium with litharge drier tended to decrease, while that with lead acetate drier showed no significant increase. It is also apparent that the initial RI is dependent on the presence and nature of driers in this formulation. The same range of media, mixed with Winsor and Newton Van Dyck Brown in linseed oil, showed further changes (not given in Table I): the RI of aged lead acetate/Van Dyck Brown samples increased to 1.533 while the corresponding litharge samples were unchanged at 1.515.

Table II shows the RI of modern paint media, both unpigmented and mixed with modern artists' oil paint for the samples described earlier. Before ageing, the RI of the paint medium dominated in each case. After ageing, the RI of the pure medium was altered in four cases out of five: two increased and one decreased. When the oil paint was also present, the shift in RI was greater, and always in the same direction of change. All samples had a significantly higher RI than new linseed oil paint and are likely to include driers, which accelerate oxidation in the paint film.

Table II. RI measurements by immersion on modern paint media, pure and mixed with Winsor and Newton Van Dyck Brown in linseed oil. Thermal ageing consisted of 34 days at 70°C and 50% RH in a climate-controlled oven. The copal medium consisted of 1:1 copal oil and drying oil with litharge (10); the others are commercial products.

Formulation	Before pure medium	Before + oil paint	After pure medium	After + oil paint
Copal medium	1.535	1.535	1.520	1.517
Maroger's medium	1.523	1.517	1.505	1.495
Oleopasto	1.507	1.505	1.515	1.535
Roberson's medium	1.527	1.525	1.533	1.535
Wingel	1.520	1.523	1.530	1.525

RI of modern samples of traditional painting materials

RI measurements by immersion and refractometry are given in Table III for a range of oils and resins used in the 19th century. Safflower oil, found today in artists' oil paints as well or instead of linseed oil, is included for completeness. The table also summarises relevant values found in the conservation literature. The low RI of beeswax can be noted in passing. Beeswax does not always combine with the other components of a paint formulation, as shown by its tendency to melt out completely on heating; hence, it can act as a matting agent by scattering light (6).

RI measurements on 19th-century paint

It soon became apparent that lead/oil primings were generally too heavily pigmented to permit RI measurement. Samples of varnish, glaze, or medium-rich paint gave credible results, although some paint dissolved after 30 seconds, which meant that the behaviour in the RI liquid had to be assessed very quickly, and re-assessed on new samples. The error on measurement of ± 0.005 was increased to about ± 0.007 when the samples showed solubility problems. Table IV shows a selection of results on suitable samples. Samples designated as "glaze" or "paint" included sufficient pigment to justify the description. The date of application of non-original varnish cannot be given with any accuracy where there is evidence on the painting or from early records and reports that the work has been cleaned and revarnished. Both early and non-original varnishes had an ultraviolet fluorescence consistent with traditional, resinous material, now well aged.

Table III. RI of pure artists' materials.

Sample	Published RI	Measured RI
Fresh linseed oil	1.48 (1)	
Linseed oil	1.482 (3)	
Linseed oil film, 10 years old	1.512 (2)	
Linseed stand oil, 1980s stock		1.489 \pm 0.003
Linseed oil, 1980s stock		1.480 \pm 0.003
Linseed oil, dried film on bottle		1.495 \pm 0.005
Linseed oil paint, c. 1300	1.57 (2)	
Lead white in oil priming, c. 1300	1.60 (2)	
Walnut oil	1.48 (1)	
Walnut oil, purchased 1990		1.478 \pm 0.003
Poppy oil, 1970s stock		1.478 \pm 0.003
Safflower oil, 1970s stock		1.478 \pm 0.003
Mastic resin, 1960s stock, dry		1.530 \pm 0.005
Mastic resin	1.536 (3)	
Dammar resin, 1960s stock, dry		1.530 \pm 0.005
Dammar resin (Batavia)	1.515 (3)	
Dammar resin	1.539 (1)	
Copal in turpentine, 1980s stock		1.488 \pm 0.003
Copal resin	1.540 (1)	
Copal, Congo	1.545 (3)	
Copal, Manilla	1.544 (3)	
Rosin	1.525 (3)	
Sandarac	1.545 (3)	
Shellac	1.516 (3)	
Copaiba balsam, 1960s stock		1.506 \pm 0.003
Copaiba balsam	1.500 (3)	
Beeswax	1.440 (3)	
Carnauba wax	1.472 (1)	

The Turner samples, or comparable material, were analyzed by gas chromatography and FTIR, as discussed elsewhere (6). Paints, varnishes, and other materials from works by the other artists were examined in cross section with an ultraviolet microscope, stained with fluorochrome and conventional stains and partly characterised by thermomicroscopy (6, 12). This gives a classification as oil-based paint or resinous/modified oil glazes. All the glazes which had a high RI have also formed severe, wide cracks that have contracted into islands and yellowed very badly. This is suggestive of modified oil paint or the use of megilps, rather than pure oil medium. The Whistler paint shows these defects only on a microscopic scale: it is somewhat younger, but more significantly, it is applied very much more thinly than that in the other paintings, all of which were completed before 1840. In fact, very few of the samples which were examined from this earlier period seemed to consist of pure oil at all, at least in the upper layers. RI measurements on Turner's paint did not give a value higher than 1.50 for paint likely to consist of oil alone. This is much less than the quoted value for very old oil paint of 1.57, and sufficiently lower than the RI of 1.53–1.55 in glazes to account for their admirable transparency. If increase in the RI of oil medium with age, in isolation, affects the appearance of oil paint, it can only be in works of must greater age than this—and it cannot be the sole cause. The selection of resinous materials and the use of varied paint formulations appears to play a greater part in the appearance of works 100–150 years old.

With a few exceptions, the resinous varnishes found on these paintings had two ranges of RI, consistent with mastic/dammar (1.525–1.527) or copal/sandarac (1.545–1.550) resins. The physical properties of the Whistler varnishes were closer to mastic, and consistent as regards RI; some of the other varnishes in Table IV with high RIs were very hard and resistant to cleaning tests, and may

Table IV. RI measurements by immersion on 19th century painting materials. Measurement error was ± 0.005 , unless stated otherwise. All works are in the Tate Gallery, London (17).

Sample	Type	RI	Date
Ashmolean palette Turner	resinous	1.490, 1.500 1.500, 1.485	post-1814
N05507R Turner	oil only	1.497	post-1814
	resin	1.520	
	oil + resin	1.527	
	oil + resin + beeswax	1.527	
N00375 Briggs	sky glaze	1.555	exh 1826
	orange	1.547	exh 1826
	green	1.550 ± 0.007	exh 1826
	varnish	1.547	applied 1872
N00337 Hilton	glazes	> 1.52	exh 1828
	varnish	1.525 ± 0.007	applied 1872
	2nd varnish	1.545	applied 1876
N00389 Jones	blue glaze	1.550	exh 1832
	brown glaze	1.545	exh 1832
	varnish	1.55 ± 0.007	original
	undried varnish	1.540	applied 1867
N00338 Hilton	priming	1.515	exh 1833
	varnish	1.525	applied 1863
N00342 Callcott	priming	1.475	c. 1830-40
	paint	1.500	c. 1830-40
	varnish	1.525	non-modern
N00432 Ward	glaze	1.55 ± 0.007	1847
	varnish	> 1.54	early
N03418 Whistler	white impasto	1.527	1864
	glaze	1.527	1864
	varnish	1.527	early or original
N01959 Whistler	white paint	1.527	c. 1872-5
	varnish	1.527	early or original
N00487 Turner	varnish	1.535 ± 0.007	non-modern
N00461 Turner	varnish	1.525 ± 0.007	non-modern
N00463 Turner	varnish	1.527	non-modern

be copal. One varnish merits further study. It appears to have been applied in the 1860s and yet has never dried properly: it has flowed down the surface of the Jones to form a thick, soft bulge at the lower edge, and cannot be said to be a typical 19th century varnish! This painting is severely cracked, and most of the others have disfiguring cracks. Documentary evidence has been found that drying problems were attributed directly to the first application of varnish, even ten or twenty years after painting (5).

The Whistler paint could well consist of copal, mastic and turpentine, a medium which Whistler described during his lifetime and claimed to use. "Copal" was such a varied product in the 19th century that its identification in the presence of other components is problematic (18).

Discussion

From these measurements, there is little evidence that the RI of pure oil paint increases sufficiently to account for observed changes in transparency of 19th century works, though it may increase significantly in older paint. The original use of resinous glazes, megilps and other paint formulations accounts for the present relatively high RI of these areas, and no evidence is available for an increase in the RI of these materials over 100-150 years, for example, in mastic-

like varnishes. The RI of modified oil paint in general depends in a complex way on the presence of lead (or possibly other) driers, the presence of pigments (which themselves affect the rate of drying), and the stage of drying or deterioration of the paint film. Generalisations from the behaviour of pure oil paint films may not be applicable to 19th century paint films, which have varied formulations.

The subject demands further investigation from several angles. Ultraviolet-free analysed samples of pure oil paint and modified oil paint from earlier centuries should be examined, as well as modern paints submitted to combinations of heat and light ageing. (Light ageing alone tends to inhibit the drying of pure oil films, which implies a poor correlation with natural ageing processes and furnishes sticky samples with a tendency to imbibe dust, unsuitable for many measurements or analyses.)

The immersion method itself could be investigated. Although it is easy to observe gross swelling of the sample in RI liquids, which are mixtures of two solvents (at least in the RI range used here) selective absorption of one solvent by the sample was noted as a possible source of error by Laurie (19). For a more comprehensive study, it would be necessary to use alternative solvents for RI measurement to eliminate this effect from consideration and to deal with samples soluble in the usual RI liquids.

It would also be useful to study the effect of pigment concentration and the role of lead and other driers. It appears that these minor components of the paint film may have a major effect on its optical properties both when new and after ageing: could these components also be affecting yellowing, solubility, or propensity to shrink and crack?

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Katherine Ara, now at the National Museums and Galleries on Merseyside, prepared and aged all the samples of modern and 19th century paint media while working at the Tate Gallery. Members of the Conservation Department at the Tate made paintings available during their conservation, and discussed painting practices in the 19th century, as has Dr. Leslie Carlyle of the Canadian Conservation Institute. Stephen Hackney, Thomas Learner and Anna Southall made helpful comments on the manuscript. The work on Turner paint samples was funded by the Leverhulme Trust.

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Working Group 17

Lighting and Climate Control

Eclairage et contrôle du climat



Abstract

The Courtauld Institute Galleries moved to a renovated 18th-century building in 1990. Financial constraints and shortage of space had prevented the installation of a conventional air-conditioning system. Initially, the large number of visitors caused a steep rise in temperature, relative humidity, and carbon dioxide levels in the un-ventilated rooms. The solution, which was finally agreed upon, combined ventilation through the old chimneys, and dispersed humidifiers and dehumidifiers linked together by computer control, which improved the climate in the building. This approach increased visitor comfort by reducing CO₂ levels, and improved environmental stability for the paintings through better control of humidity.

Keywords

Historic building, sealing of rooms, relative humidity, temperature, carbon dioxide emissions, chimney fans, particulate matter, building management system



Figure 1. The north front of Somerset House.

A Pragmatic Approach to Environmental Improvements in the Courtauld Institute Galleries in Somerset House

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A description of the renovated building and its effect on the internal climate

The Courtauld Institute Galleries' collections are housed in the Fine Rooms of Somerset House, begun by Sir William Chambers in 1775 (See fig. 1). The site lies between the Thames and the Strand, a busy road which the northern rooms overlook; to the South is a large inner courtyard. The Fine Rooms were designed for three learned societies—the Royal Academy of Arts, the Royal Society, and the Society of Antiquaries—and comprise a suite of four large meeting rooms and two smaller rooms on the first floor and five rooms on the second floor (See figs. 2, 3). Of these second-floor rooms, the largest by far is the Great Room (Gallery 8), a lofty chamber with clerestory windows intended for exhibitions. The rooms on the first floor are arranged in two parallel interconnecting suites along an East-West axis, and are lit with large sash windows. The Courtauld Institute, together with its collections, moved into these rooms and the adjoining wings in the Autumn of 1990, following a major renovation project.

The building is of stone with brick on the inside, lined with lath and plaster, and has wood floors (those in the galleries are now largely carpeted). During the renovations, the gallery windows were provided with secondary glazing as part of the measures designed to isolate the interior from the fluctuations in ambient external temperature and humidity (1).

The secondary glazing was very effective in reducing air leakage. Together with the building's substantial construction, this provided an essentially stable environment during the commissioning period before the admission of the public. What the building ultimately proved unable to do, was cope with internally generated moisture and heat. Another consequence of the sealing of the building to stabilize conditions, was that once the rooms had warmed up, they would rarely cool by more than 2–3° overnight. This occurred both in the winter and summer, and only Gallery 8 would, in cold weather, prove an exception. With its considerably greater ratio of air volume to solid structure, fluctuations in temperature tended to be considerably greater.

Full air-conditioning had been considered during the planning stage of the project, but had been ruled out, not only on grounds of cost, but also on account of the constraints imposed by the building. There is little room for plant and ductwork and the building's importance makes any proposed alteration to the fabric controversial.

The Galleries were opened to the public in mid-June, 1990, with a fanfare of publicity that brought unprecedented numbers of visitors. There were 1727 visitors on the first day, a pattern which continued for several weeks. As a consequence, temperature and RH rose dramatically during opening hours. This process may be seen in Figures 4 and 5, in which the readings for gallery 5 are compared with external conditions. Water vapour produced by visitors created a rise in water vapour concentration. There is a tendency for water vapour concentration indoors and outdoors to equalize; in this case, because of the large

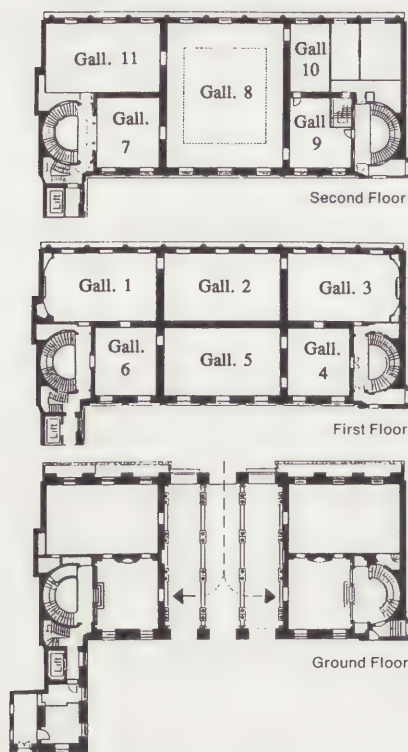


Figure 2. Plan of the Courtauld Institute Galleries.

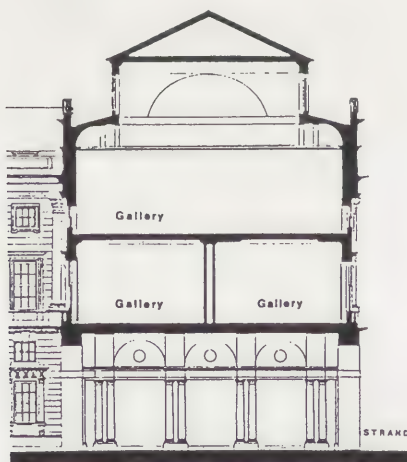


Figure 3. Cross section of the Galleries.

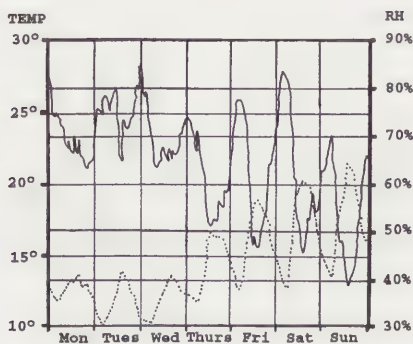


Figure 4. Ambient readings starting at 0 hours on 11th June 1990 at the Meteorological Office (Holborn Weather Centre).

number of visitors and because the Galleries had been sealed, the internal water vapour concentration soon became greater than that outside.

Proposals to improve environmental conditions

A Project Team was, therefore, set up to evaluate the options for improvement (2). It was acknowledged that there was no exact precedent to follow, and that a solution had to be found to improve the environmental stability for the collections, as well as provide healthy and comfortable conditions for visitors and staff. The solution would also need to avoid undue stress to the fabric of the building. Two options were discussed, one of which relied on centralised air conditioning, the other on decentralised control with equipment dispersed throughout the building. The first option consisted of an air-handling plant on the roof which would deliver filtered air at the correct relative humidity to the galleries below via the flues serving the redundant fireplaces. In addition, the existing low pressure hot water heating system would be replaced with cooling units.

The second option aimed to enhance the natural tendency of air to move up through the building (stack effect) by placing fans on top of the chimney stacks to draw air out of the galleries. Air would be drawn into the galleries through the gaps around the closed doors. The speed of the fans would be controlled by carbon dioxide monitors measuring the level of CO₂ emissions present in each room (3). Control of relative humidity would still be required; steam humidifiers and dehumidifiers linked to remote humidistats formed part of this proposal. This equipment would be controlled by a Building Management System (BMS) to reduce the amount of supervision required and avoid the real possibility of individual humidifiers and dehumidifiers, each fitted with independent control sensors, operating simultaneously.

Evaluation of the options

The Galleries' Subcommittee had early on expressed its determination that the first objective was to find the right solution and then to set about financing it. What was harder to foresee was that no single solution would answer all the problems and that compromises would have to be reached. Particular reservations were expressed about the partial air conditioning option, due to the disruption to the fabric of the building that installing pipework for the coolant would entail so soon after the completion of the renovation. The Subcommittee, therefore, decided that this option would be seen as a longer term solution to be postponed until the success of the more passive approach could be evaluated.

The decentralised control option was adopted, with modifications. The steam humidifiers were omitted because evaporative humidifiers were already installed and provided adequate control.

In the consulting engineers' view, the increase in the ventilation rate (by a factor of four) would not greatly lower the temperatures during a warm summer and the rooms would continue to heat up. This would still cause some discomfort to the public but, in the view of the conservation consultants, was unlikely to endanger the paintings if humidity control could be achieved.

Tender documents were sent out late in May 1991. The work was started in August and the system became fully functional at the beginning of November 1991.

The new system and its control

The new system consisted of three components: humidifiers and dehumidifiers, chimney fans, and a Building Management System (BMS).

The system already in use consisted of one evaporative humidifier in each of the five smaller galleries, two humidifiers in the four larger first floor galleries, and four in Gallery 8 (See fig. 6). The evaporative humidifiers have a humidification capacity of 1–2.1 litres per hour (depending on the fan speed), which is sufficient, according to the manufacturers' specifications, for a room up to 1000 m³ in volume (4).

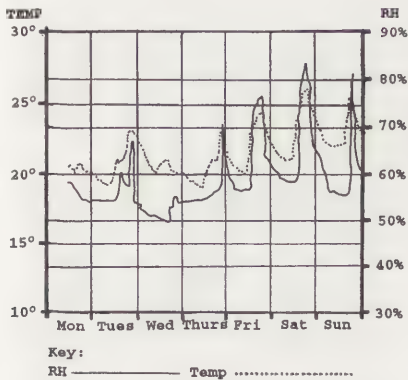


Figure 5. Ambient readings starting at 0 hours on 11th June 1990 at Gallery 5.



Figure 6. Gallery interior with humidifier and dehumidifier.

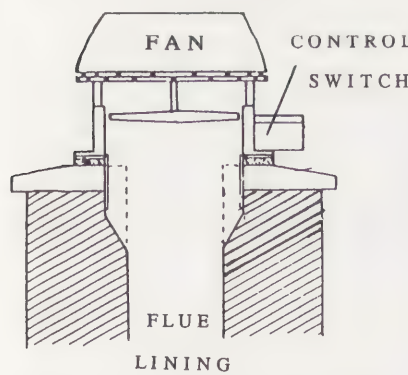


Figure 7. Cross section of chimney fan.

The Project Team decided to add an equal number of dehumidifiers, with an extra two, in Gallery 8 (See fig. 6). The model chosen has, according to the manufacturer's specifications, a moisture extraction rate of 9.5 litres per 24 hours (5).

The new ventilation system required that the 17 chimney flues be unblocked and lined with ductwork of 175 mm in diameter. Tubular chimney fans with variable speed motors were installed on top of the flues and their operation was also linked to the BMS (See fig. 7) (6). The fan speeds are determined by the level of CO₂ emissions detected by the sensors in each gallery. The sensor consists of a length of plastic tubing through which samples of air are pumped from each gallery to an indoor CO₂ monitor (See fig. 8).

In order to provide a more reliable means of controlling the humidification and dehumidification equipment, each gallery has been provided with a combined humidity and temperature sensor linked to the BMS (See fig. 8). The control outstations receiving this information process it and, if necessary, send a command over the electrical mains supply to the equipment located in the galleries. Each piece of equipment has a small control unit connected to it, in parallel with the integral humidistat, which responds to the commands given by the outstation that switches the unit on or off. The control unit will also acknowledge that it has received the signal.

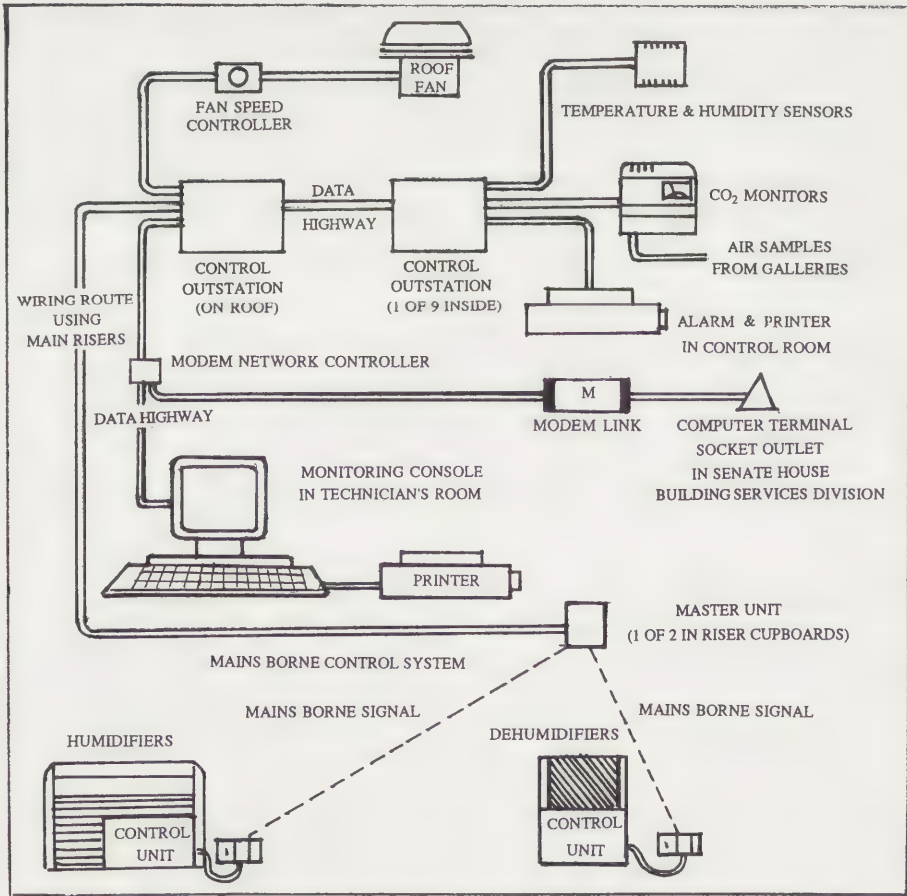


Figure 8. Schematic diagram of environmental control system.

Central to the operation of the BMS is the computer monitoring console, which provides a window for a display of events and a means of altering environmental parameters (8). It also allows the setting up of certain functions, such as printed statistical or graphic reports of the conditions recorded over a given period.

The system's performance during the first year of operation

It is now possible to draw some conclusions about the system's ability to improve control over CO₂, RH, and temperature levels. The test of the system was whether it had been successful in improving ventilation without destabilizing RH.

Human thermal comfort was a concern. As anticipated by the consulting engineers, excessively high temperatures recurred in the summer. Increasing the ventilation rate from approximately 0.25 air change per hour to 2 air changes per hour did not produce a noticeable cooling effect, even though the summer of 1992 was not nearly as hot as that of 1991.

External conditions between June and August 1992 measured in the range of 16.5–32°C. Ambient temperature in the first-floor galleries rarely fell below 24°C and generally rose by 1–2° during the day. Galleries 8 and 11 tended to be the warmest, with the maximum temperature of Gallery 8 usually 1° higher than the rest of the second-floor galleries. The minimum temperature of Gallery 11 was generally higher though more stable. The elevated internal temperature appeared to be a result of external and internal heat gains during the day, the thermal mass of the building, and the overnight shutdown of fans.

Although temperatures rose regularly to a maximum of 26°C, the stuffiness and stale air, which had been acute previously, disappeared. Information is still being gathered on the appropriate setting for the fans. The original calculations estimated that the fans would be capable of providing up to 2 air changes per hour, which is double the current design practice in the United Kingdom for naturally ventilated buildings (9). It was calculated that this would enable CO₂ levels to be kept below 1000 ppm in the galleries, assuming a maximum occupancy of 500 persons at any one time. This may be compared to the maximum concentration of 3000 ppm of CO₂ measured in the unventilated galleries in November 1990. Taking Gallery 5, much frequented because of its Impressionist paintings, as an example:

Date	CO ₂ (ppm)	Ventilation rate	Temp	Visitors
22–30 Nov 1991	3000	0.22–0.39 ac-h	20–22°C	5158
22–30 Nov 1992	1090	approx. 2.00 ac-h	20–22°C	1956

One of the main objectives during the summer of 1992 was, therefore, to introduce adequate ventilation into the galleries. This was achieved in practice by setting low CO₂ thresholds. The setpoint at which the CO₂ monitors triggered the fans was adjusted to 25–100 ppm above the overnight background level. The period during which the fans could come on at all was limited by a timer to a maximum of 15 hours per day, from 9 am to midnight.

Environmental improvements for the collection

The original aim of achieving environmental stability by sealing the building showed that this could not be achieved exclusively by passive controls, using the thermal mass and hygroscopic properties of the building fabric. The walls are made of stone with brick on the inside, lined with lath and plaster which is finished with a water-based emulsion paint. Instability was worse in the summer, especially during the time the space was occupied. The summer of 1992 provided the first opportunity to test whether a balance had been struck between the thermal comfort needs of people and the environmental requirements of the collections.

Gallery 5, which has been discussed earlier, is selected again as an example (See fig. 9). In June 1992, diurnal CO₂ levels increased after 10 am when the Galleries opened to the public for the day. CO₂ typically peaked in the middle of the day and declined after 6 pm when the galleries closed for the day. The early afternoons proved to be the most unstable period with CO₂ increases of 200–400 ppm in all galleries, but rarely exceeding the 1000 ppm threshold. RH and temperature fluctuated, too, during the periods of high CO₂ instability, caused by the fans switching on and off. These coincided with periods of high occupancy and the greatest intake of fresh air through mechanical ventilation, when RH and CO₂ fluctuations followed a similar pattern of change. While RH stabilized at night when the galleries were closed, both CO₂ and temperature levels

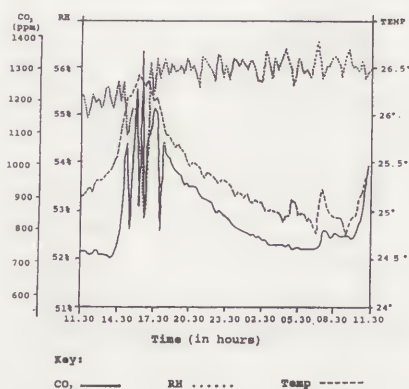


Figure 9. Representative RH, temperature, and CO₂ in Gallery 5 for a 24-hour period in June 1992.

gradually fell from their afternoon peak but started to rise the next morning. The significance of these changes can only be seen in comparison with the conditions that existed in June 1990 when the Galleries first opened. In June 1990, the RH fluctuated between 50 and 85% and the temperature range was 19–26°C (See fig. 5). In June 1992, RH fluctuated between 53 and 56.5% and the temperature range was 24.75–26.5°C, so that while ambient temperature remains high, RH control and the level of comfort experienced by the occupants of the galleries has been improved (See fig. 9). Although there were some discrepancies between the galleries, the improvement applied throughout the galleries. The BMS managed to maintain ambient relative humidity within the design parameters of $55 \pm 5\%$.

The level of particulate matter in the Galleries

Apart from the risk of RH instability, another consequence of increasing the air change rate, is that particulate matter is drawn into buildings and deposited on their contents. In February 1991, measurements of respirable mass concentrations (the mass concentration of smoke, fumes, dust, and other airborne particles small enough to be inhaled) in selected zones of the Galleries and their immediate surroundings had been carried out (10). In November 1992, similar measurements were repeated in the same locations and at approximately the same time and with the same type of equipment, first with the fans which had been installed after the first set of measurements off, and then with the fans running at full capacity (11). Other than the installation of mechanically assisted ventilation in the Galleries, no other changes had been introduced in the building which could have affected the level of indoor particulate concentrations. The measurements are compared below:

Date	Highest reading (mg/m ³)				Mean of readings (mg/m ³)			
	Roof	2nd Flr	1st Flr	Ext.	Roof	2nd Flr	1st Flr	Ext.
Feb 1991	0.14	0.10	0.08	0.22	0.10	0.06	0.05	0.11
Nov 1992								
Fans off	0.07	0.05	0.08	0.07	0.04	0.04	0.05	0.06
Fans on		0.05	0.10			0.04	0.14	

With the fans switched on, Galleries 1 and 2 on the first floor, nearest the entrance, had the highest particulate concentration, considerably higher than with the fans switched off. The readings from the second floor were identical whether the fans were switched on or off, but lower in 1992 than in 1991. This may be explained by the lower external respirable mass concentration in 1992 in comparison to 1991. Evidence from other internal environments suggests that by and large dust concentrations inside are generally a little lower than outside (12). This relationship is altered by the operation of the fans. Only identification of particle composition and size would establish whether the fans are drawing in dust from outside or driving dust from interior sources into the air.

Future action

Adjustments and minor improvements to the existing control system are continuing. Modifications are planned to the BMS software to ensure that the fans do not operate should relative humidity fall beneath a specified level. External humidity and temperature sensors will be fitted to facilitate a comparison between external and internal conditions. A steam humidifier linked to the BMS is to be installed near the main entrance to the Galleries at street level to reduce fluctuations in the stairwell which can effect the RH stability in the adjoining galleries. A direct link between the Building Services Division of the University and the BMS at the Galleries will be set up by modem and a telephone line. An alarm and printer linked to the BMS will be installed in the Security Control Room for 24-hour supervision.

Conclusions

Full air conditioning was not a viable option for the Courtauld Institute Galleries. The environmental control solution finally adopted balanced the needs of the historic fabric, those of its valuable contents, and the comfort of staff and visitors. To achieve this, the Building Management System played an essential part in synchronising the equipment dispersed through the galleries. CO₂ levels were reduced to acceptable limits, and relative humidity brought under better control.

Acknowledgements

We are grateful for the co-operation of Firmstone and Co, architects, F.C. Foreman and Partners, consulting engineers, and Concord Temperature Controls Ltd, installers of the BMS, and for their continuing interest in the project.

Notes

1. M. Cassar, "Controlling the Environment in Museums in the United Kingdom with Special Reference to Relative Humidity and Temperature" (M.Sc. Thesis, University College London, 1991).
2. Project team: Director of the Galleries; Firmstone and Company, Walcot, Charlbury Oxford OX7 3PQ, architects of the main project; F.C. Foreman and Partners, 17, Grosvenor Gardens, London SW1 0BD, consulting engineers; Chief Engineer of the University's Building Services Department; external advisers: the Bartlett School of Architecture and Planning, University College London, Wates House, 22, Gordon Street, WC1W 0QB; the Environmental Adviser to The Conservation Unit of the Museums and Galleries Commission, 16, Queen Anne's Gate, SW1H 9AA, co-author of this paper; the Adviser for the Conservation of Paintings and Environmental Control to the National Trust, 36, Queen Anne's Gate, London SW1H 9AS. The Galleries' paper conservator, co-author of this paper, represented the Galleries' interests and acted as co-ordinator.
3. Indoor CO₂ monitors (Model APBA 250E), manufactured by Horiba Ltd., Miyahigushi Kisshoin Minami-ku, Kyoto, Japan.
4. Defensor PH26, manufactured by Defensor AG of Switzerland and supplied by Air Treatment Technology, Fecon House, Garth Road, Morden, Surrey SM4 4LG, United Kingdom.
5. Tremdri TCH4, manufactured by Air Trembath, Felstead Road, Longmead, Epsom, Surrey KT19 9XS, United Kingdom.
6. RS 330 Exhausto Tubular Chimney Fan, supplied by R&S Cartwright (Manchester) Engineers Ltd., Floats Road, Roundthorn, Manchester M23 9NE, United Kingdom.
7. Trend 921 Direct Digital Control Building Management System supplied and installed by Concord Temperature Controls Ltd, Concord House, Providence Drive, Providence Street, Lye, Stourbridge, West Midlands DY9 8HQ, United Kingdom.
8. The Tandon 286-N monitor and Epson LX-850 dot matrix printer were supplied and installed by Concord Temperature Controls Ltd.
9. CIBSE Guide Vol. A, Design Data, The Chartered Institution of Building Services Engineers, 1988, A4-14.
10. I.N. Potter and P.D.R. Potter, *Courtauld Galleries, The Strand: Measurement of Respirable Mass Concentrations*, Report No. 67580 No. 1, February 1991.
11. TSI Piezobalance Respirable Aerosol Mass Monitor Model 8510. TSI Inc, TSI Corporate Headquarters, 500 Cardigan Road, PO Box 64394, St. Paul, MN 55164, USA. Supplied in the UK by BIRAL (Bristol Industrial & Research Associates Ltd., PO Box 2, Portishead, Bristol, Bristol BS20 9JB, United Kingdom. The monitor measures the mass concentration of smoke, fumes, dust, and other airborne particles present in the sampled air.
12. P. Brimblecome, "Particulate material in air of art galleries", in *Dirt and Pictures Separated*, United Kingdom Institute for Conservation of Historic and Artistic Works, 1990.

Abstract

Heavy demands are made today on the indoor climate in storerooms of museums and archives. These demands have resulted in increasingly advanced air-conditioning plants with high initial costs and on-going operating expenses. The control and maintenance of the installations are so difficult that often it is impossible to maintain the specified indoor climate. A Swedish-Danish research and development collaboration was established in order to map the thermal values and humidity of the outdoor climate, the building, the indoor climate, and the storage areas. The state archives of Schleswig-Holstein are stored in unventilated, well-insulated rooms that are heated to maintain an almost constant relative humidity, buffered by the archives themselves.

Keywords

Museums, archives, indoor climate, relative humidity, natural climate control, Regional Archive of Schleswig-Holstein (Germany), Zephyr climate control

Resource-Saving Storage of Historical Material

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Introduction

Historic material can be stored in a basement under Cologne Cathedral in a good state of preservation for several hundred years. Why is it today necessary to store museum objects, art, and documents in storerooms with very tight specifications for relative humidity and temperature, maintained by advanced and expensive air-conditioning installations?

Demands on indoor climate in storerooms

In connection with the storage of art and historic objects, standards for the past several years indicate different guidelines for different material categories. "Standard" should in this connection be understood in a wider sense than national or international standards, and comprises guidelines as well as customs described in the technical literature on museums.

As a result of the increasingly restrictive demands in these "standards," modern buildings for storage and display of museum objects and documents have been provided with extremely complicated air-conditioning plants. The plants have sometimes succeeded in maintaining the stipulated values within the specified limits. There is, however, a very great penalty in installation and running costs for advanced mechanical air-conditioning plants. Generally, detailed scientific reasons for the formulation of the mentioned standards are missing, e.g., the stipulated demands on climatic parameters and their tolerances.

In spite of these technological efforts, there is no overwhelming evidence that a perfectly steady climate is necessary for the stability of the objects.

Complete climate control

The use of advanced air-conditioning plants in storerooms also demands advanced supervision and maintenance programs to ensure that the plants operate according to their purpose. The systems for automatic control of these plants, particularly the humidity sensors, demand cleaning and calibration at regular intervals. These air-conditioning plants are often so complicated that even the daily supervision of the plant demands a specially educated staff. Thus, besides heavy initial expenses, considerable operating expenses are also involved, such as those for staff, energy, and service. As the management often attempts to reduce these expenses, the actual climate may eventually become much worse than that specified.

With a well-functioning plant, the relative humidity can be kept within narrow limits, but in some periods a dehumidification and a humidification will alternately take place. The relative humidity will, therefore, zigzag within the stipulated limits. The short, rapid changes are transmitted to the stored objects and cause tensions between the surface of the objects and the material below. The result of the varying tensions is that the surface loosens or crumbles.

"Natural climate control"

Natural climate control is an idea that consciously utilizes building physics and the local climate in order to form a building envelope which is able to moderate the influence of the outdoor climate on the indoor climate. Moreover, natural climate control takes place without the use of air-conditioning plants in the full sense. However, heating plants and mechanical ventilation might be used.

Table 1. Specified indoor climate in the storerooms in Schleswig, Germany.

Month	Temperature	Relative humidity
January	12°C	40%
February	12°C	40%
March	13°C	40%
April	13°C	50%
May	16°C	55%
June	19°C	55–60%
July	22°C	55–60%
August	22°C	55%
September	20°C	55%
October	17.5°C	50%
November	13.5°C	50%
December	13°C	45%

Moderating the influence of the outdoor climate on the indoor climate demand that the air changes be kept at a minimum; this utilizes the buffer effect of the building on the moisture content and air temperature.

The Regional Archive of Schleswig-Holstein, Germany

The Prince's Palace (Prinzenpalais) in Schleswig is the home of the Regional Archive of Schleswig-Holstein. The Prince's Palace has in recent years been subject to a comprehensive rebuilding and renovation. In that connection, 10,000 m² of new storage rooms distributed on four stories have been built. Special objects, such as photos and films are stored in climate-regulated storerooms, but most of the archives remain in rooms with natural climate control.

Schleswig has a temperate coastal climate that varies from –6 to 21°C (21 to 70°F) with 50 to 100% relative humidity. The specified indoor climate varies through the year as shown in Table 1.

This climate is achieved by a combination of factors. Most of the stability is provided by the building which is airtight, insulated, and thick walled (See fig. 1). The pattern of use is infrequent entry and intermittent use of lights, which contributes to climate stability. The fine adjustments are made by heating.

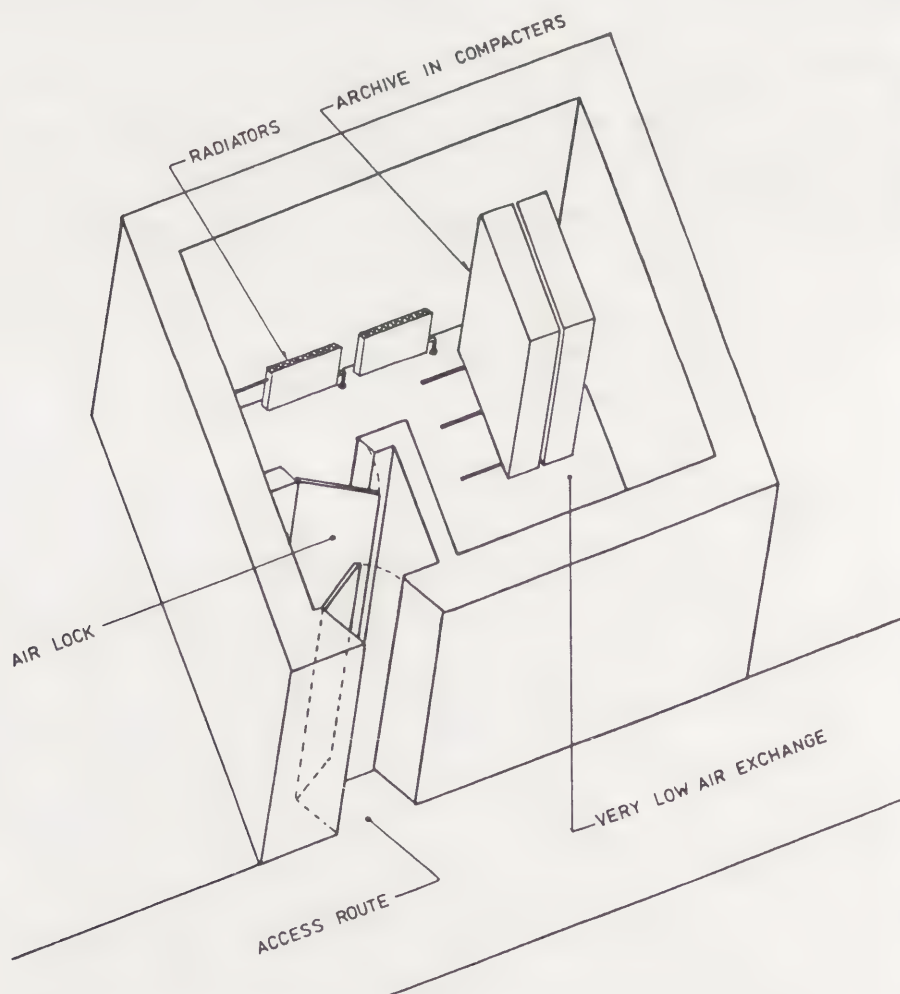


Figure 1. Principal drawing of the storage rooms in Schleswig.

The stores are constructed without windows and with 800 mm thick walls (See fig. 2). The outer face of the wall is a 150 mm brick wall to protect against rain and solar radiation. Between the brick wall and the insulation there is a 60 mm-slot ventilated with outdoor air. The insulation consists of a 200 mm thick layer of mineral wool. The inside part of the outer walls consists of 400 mm of massive brickwork, which is also the bearing structure and acts as a thermal and hygroscopic buffer. The inner walls between the storerooms and the access area are like the outer walls, but without the ventilated slot.

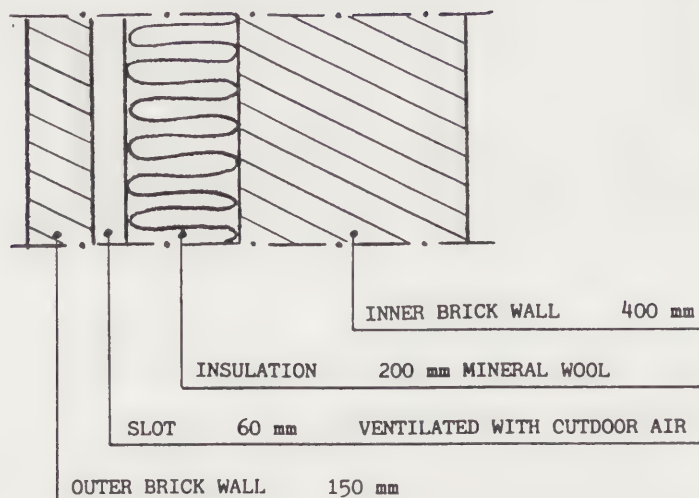


Figure 2. Sectional view of the outer wall.

A consequence of the large dimensions of the brickwork was that in order to dry the rooms to the correct equilibrium, the rooms had to remain empty for two years before being put into service. This dehydration period, during which the stores were heated and ventilated, was very important because when the stores are in service there are no possibilities for dehydration in this airtight building.

Today, the stores work with a very small air exchange. The low air exchange is due to the tight construction, but also to air locks having been established at all entrances to the stores.

The energy consumption of the stores is very low because of the well-insulated and tight construction. Energy saving lamps assist in avoiding unwanted temperature increases.

Conclusions

A research collaboration was established between the Technical University of Lund in Sweden, The Danish National Museum, and the Danish consultants and planners, Birch & Krogboe A/S. The aim of the research project, financed by Birch & Krogboe and by Nordic Industry Fund, was to develop a resource saving concept for the establishment of a climate suitable for the storage of objects.

This research project was a result of the growing scepticism of museum conservators as well as museum and archive managers towards the traditional solution of complete climate control. It is the first attempt to combine the existing knowledge of objects storage with the principles of building physics. We have entitled the project ZEPHYR. Zephyr, the west wind, was worshipped as a god of the ancient Greeks and Romans. The west wind blows in that part of the world from the sea, and creates well-being because its temperature and humidity are constant. Thus, it moderates the climate by being warm in the winter and cool in the summer. It was precisely this buffer effect that we desired to take advantage of in the case of "natural climate control."

The scientific aim was to map the interaction between the building physical qualities of a storeroom and the material physical qualities of the objects being stored. Models will be developed that describe the interactions of the outdoor climate, the building, the indoor climate, and the stored objects. At the same time, the scientific basis for the existing standards will be evaluated.

On the basis of the knowledge gained regarding the interaction between store-rooms and the stored object, concepts for the design of storerooms and stores will be developed, in which an appropriate climate is obtained with low energy consumption, low operation and maintenance efforts, and for which the initial and operating expenses, in a total economic perspective, are optimal.

The wish to collect, preserve, and store art and historical relics for the benefit of the future demands a storage climate that, of course, allows minimal decomposition of the objects and is economically defensible.

The goals of this project are of international interest. The young nations of the world are very conscious of the historical dimension, and consequently national museums are being built. However, economic resources for new buildings are limited. The efforts of this project are directed towards less expensive alternatives.

Abstract

A study of the walls of a medieval church shows that porous, water absorbent materials such as lime plaster and porous limestone will provide effective short- and medium-term humidity buffering in a room with about one quarter of an air change per hour. The church also has natural humidification. The source of the water vapour is probably ground water evaporating from the saturated lower part of the wall. The porous brick floor also contributes to the humidification. Architects can adapt some aspects of church architecture to improve climate stability in museums.

Keywords

Relative humidity, buffers, church, heating, environment



Figure 1. Gundsømagle church, near Copenhagen.

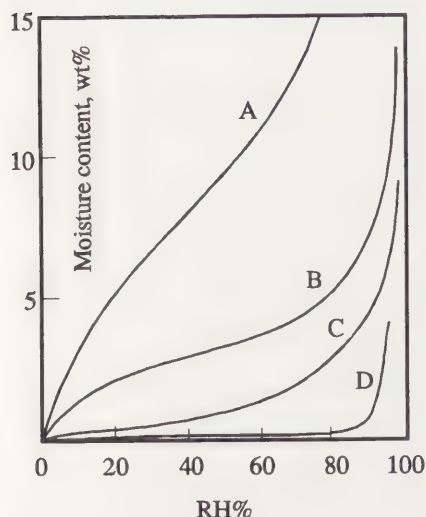


Figure 2. Absorption isotherms of materials mentioned in the text. A: Wood. B: Lightweight concrete. C: Medieval lime mortar. D: Calcareous tufa.

The Use of Porous Building Materials to Provide a Stable Relative Humidity

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Introduction

This is a study of the stabilising effect on relative humidity (RH) of porous walls and porous surfaces within buildings. Our inspiration and our evidence comes from a study of the microclimate in a church at Gundsømagle, near Copenhagen (See fig. 1). The church and its wall paintings are described in another article in these preprints (1). Here we tell only enough about the church to explain our argument that porous, hygroscopic wall surfaces are a valuable, though seldom used, aid to climatic stability in museums.

The church also enjoys passive humidification during the winter. The church is heated to 12°C, but still maintains over 60% RH inside at times when the expected value, based on the water content of the outside air, would be about 30%. The source of this humidity is probably the saturated lower part of the wall, but there is a contribution from the porous brick floor.

The structure

Gundsømagle church was built soon after 1100 (2). The walls, 0.8 m thick, are made from blocks of a very porous, calcareous tufa. The surface coating on the outside of the church is a thin layer of hydraulic lime mortar covered with limewash. The inside of the church is mostly covered by medieval lime plaster 3–12 mm thick. There is also much modern plaster of the same approximate composition: three parts quartz sand and one part calcium carbonate. The ceiling vaults are of brick, coated on the underside with lime mortar. Most of the floor area is new porous brick, laid over a porous base of lime mortar and insulating mineral pellets. This layer permits water vapour transport from the earth below.

The church interior

The volume of the church is 600 m³. The wall and vault area is 400 m². The wooden furniture is mainly painted, but the underneath surface of the seats is bare wood, and the floor under the seats is constructed of wood treated with calcium soap to reduce its porosity and dirt uptake. In winter, the church is warmed to 12°C by electric heaters under the seats. For church services, the temperature is temporarily and rapidly raised to about 20°C. One other piece of information that we need is the air exchange rate. This is about 0.25 air changes per hour. It was measured over a five week period using fluorinated tracer gases.

Hygrometric properties of the materials

One can regard the church as basically a box made of porous inorganic materials resting on bare earth. The main materials (lime mortar, limestone, and brick) have a rather small absorption of water at moderate levels of relative humidity, compared with wood or silica gel but, as we shall see, their exposed area and

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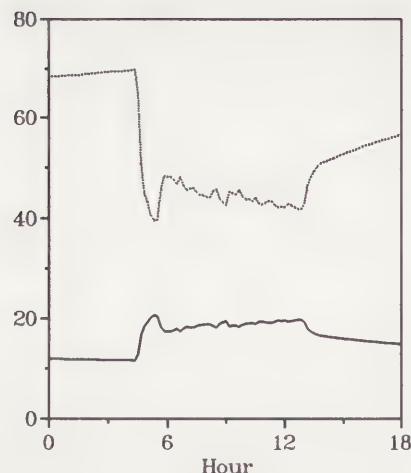


Figure 3. Actual temperature (solid line) and expected relative humidity (dotted line) in the church, 14 April 1991. The RH is calculated from the water vapour content of the air before warming, acted upon by the actual temperature through the day. This corresponds to the RH expected in a building entirely unreactive to atmospheric water vapour.

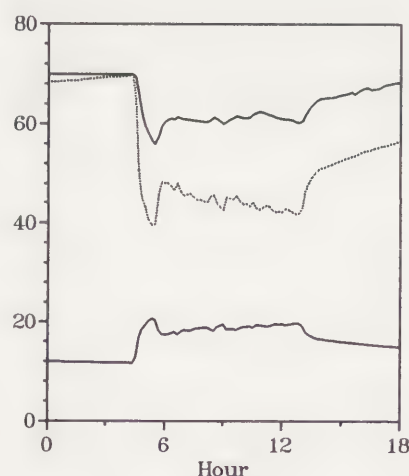


Figure 4. The same data as in Figure 3 with the measured RH added (solid line). Note that the fall in RH during the warm period is only a third of that expected for an inert room.

their bulk compensate for the small buffer capacity (See fig. 2). The main hindrance to free movement of water is probably the hydraulic mortar on the outside of the wall.

The permeable wall is a distinguishing feature of Danish churches, although most churches are of porous medieval brick rather than the rare lime tufa of Gundsømagle. Secular buildings of such permeability to water vapour are now rare. Limewash (a brushed-on suspension of calcium hydroxide in water that dries to a thin layer of calcium carbonate) is still a common exterior finish for old buildings in northern Europe, but the inside wall surface is very often painted with relatively impermeable modern acrylic or oil paint. Modern building practice has moved towards totally impermeable walls with a polyethylene air barrier close to the interior surface.

The main point of interest in this article is how well the simple, ancient, porous wall performs in contrast to the many failures of complicated modern walls with air barriers (3). It is true that these failures occur in warmer buildings than the church we describe here, but we think that the concept of the homogeneous, hygroscopic wall is worth re-evaluating for museum structures.

We have been fortunate in the choice of Gundsømagle church for our experimental work. The original objective was to study the effect of the heating system on the stability of the wall paintings. The heating system, with its sharp changes of temperature before and after church services, has proved ideal for studying the various factors affecting the microclimate.

Moisture buffering by the walls

We can explain how the church walls control the RH by following the climate on one day (April 14, 1991) when the church was warmed from 12°C to about 18°C for the comfort of the congregation. We start by predicting what the RH would be if all the church walls and furniture were entirely unabsorbent. The dotted RH curve in Figure 3 is a calculated value derived from the water content of the inside air just before the temperature rise, combined with the actual temperature throughout the day (lower line on the graph) to give the expected RH, assuming no absorption or desorption of water vapour.

What actually happened to the RH that day is shown by the top line in Figure 4. The relative humidity dropped, but less than halfway towards the calculated value, shown as a dotted line. This phenomenon is quite typical in churches (4,5). It appears that the RH is being buffered to some extent, moderating but not preventing the expected fall in RH.

We believe that the RH is actually being perfectly buffered, but at the wall surface temperature. Figure 5 shows the calculated relative humidity at the wall surface as a dotted line. This cannot be measured directly because the cool boundary layer of air is only about one millimetre thick. The surface RH is derived by first calculating the water vapour content of the air from the measured RH and air temperature in the church. This value for water vapour content is combined with the wall surface temperature (lower dotted line) to give the RH at the surface (top dotted line). The RH thus calculated holds remarkably steady throughout the warming period. This can be interpreted as a coincidence or as evidence that the wall is buffering the RH of the thin layer of air close to its surface. This air then moves away and mixes with the warmer room air, so the RH drops.

This argument is rather indirect, so we confirmed the validity of our theory by measuring the RH in a chamber sealed against the wall. This chamber is shown in Figure 6. It was set on the wall, two metres above the floor. The RH sensor in the chamber is well outside the boundary layer of cool air and is at the same temperature as the air in the church. The observed RH in the chamber is shown as a dotted line in Figure 7, together with the RH measured in the choir (solid line). The two curves almost coincide, showing that the cup is acting like a miniature model of the church, confirming that the observed RH in the church is defined by RH buffering at the wall.

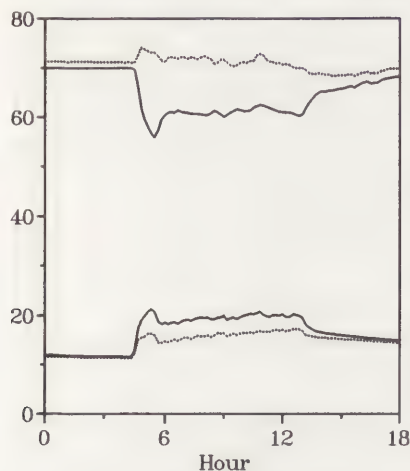


Figure 5. The calculated RH at the wall surface (top dotted line). This is derived from the measured wall surface temperature (bottom dotted line) and the water vapour concentration derived from the measured RH and temperature in the church (solid lines). The steadiness of the wall surface RH indicates perfect buffering in the boundary layer of air at the wall surface.

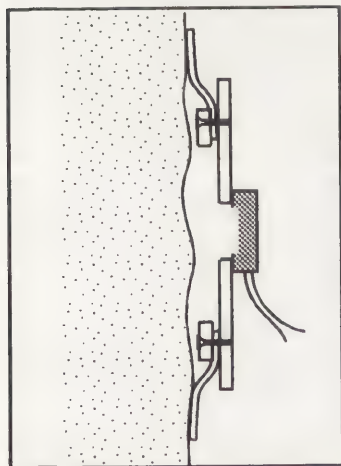


Figure 6. Cross section of the chamber used to measure the microclimate in equilibrium with the wall. The area of wall exposed within the chamber is 0.07 square meters. The RH sensor (grey) is within the chamber but at room temperature.

This evidence for buffering against the RH change caused by sudden temperature change is supported by evidence for buffering against the RH change caused by ventilation. After the service, the church is usually ventilated thoroughly. Figure 8 shows such an event. The two lower curves in this figure show the dew point of outside air (dotted line) and of inside air (lower solid line). These become nearly equal at one point, indicating total replacement of the inside air by outside air. When the door is closed, the RH (top line) rapidly returns to its original value.

This is our evidence for rapid and effective buffering of the interior RH by the large expanse of porous wall. It is probable that the brick vaults also contribute to the buffering.

Long term humidity buffering by the walls

Figure 9 shows the inside (solid) and outside (dotted) temperature and relative humidity for a period of a week in summer. The stabilisation of the interior climate is impressive. Our case for the use of porous walls for humidity stabilisation is complete. Limestone tufa is a rare material in most parts of the world, but lightweight concrete is a good substitute. It has a rather steep absorption curve (See fig. 2). Bare concrete is regarded with disfavour in museums because of its tendency to release alkaline particles into the air. Fully reacted concrete does not effloresce in this way; in any case, the surface can be covered with porous wallpaper, distemper paint (pigment in a base of chalk powder with glue or carboxymethylcellulose binder), or simply lime plaster. These alkaline materials give the bonus of absorbing the predominantly acid gases that pollute the atmosphere of museums. There are traditional materials with significant buffer function. For instance, mud is a good buffer. Wood is excellent as a buffer, but it is flammable and it emits acetic acid vapour.

Humidification by porous walls and floors

Gundsømagle church enjoys a moist as well as a stable microclimate. Figure 10 shows a typical week's climate in winter. The RH stability is impressive but the inside RH is consistently higher than that attained by warming outside air to the inside temperature (dotted line). There must be some continuous source of water.

One source can be identified by a glance at the lower part of the wall inside the church: it is green with algae! The wall is saturated to about 300 mm above the floor. Water vapour also comes through the porous floor. When we put the chamber, shown in Figure 6, on the floor, the RH within it rose to 100%, indicating that the floor acts as a water vapour source, not as a buffer. The process was very slow, however. We assume that the lower wall is the source for most of the water. The observed RH is the equilibrium value resulting from competition between evaporation from the walls and air leakage from the church, with the upper parts of the walls providing buffering. The amount of water added to the church air is about 15 kg per day in winter.

There is one other possibility. There may be a transfer of the outside RH, which averages about 90% in winter, through the porous wall. In climate engineering textbooks, it is stated that water vapour will move through a porous wall in the direction that tends to equalise the water vapour pressure inside and outside, not the relative humidity. This generalisation, however, only applies to large holes and to pores which do not react to water vapour in any way. Porous limestone does absorb water vapour according to the local RH, a process that is only slightly affected by temperature. It can, therefore, be regarded as a relative humidity transmitter: water vapour moves through in the direction that tends to equalise RH within and without. The process is probably rather slow, because the RH in the chamber sealed to the wall is only slightly higher than that in the church. It seems likely that the rising damp in the walls is the main source of water vapour. Only measurements of the water vapour flux through the various surfaces can confirm our theory. We have not yet succeeded in doing this and would welcome suggestions.

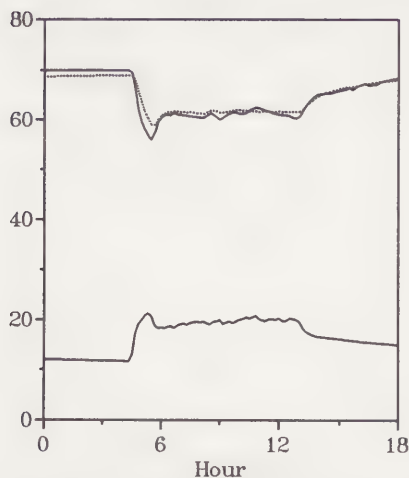


Figure 7. The RH measured in the chamber sealed against the wall (dotted line), compared with the RH measured in the free air in the church (upper solid line). The close coincidence of these values supports the theory that the RH in the church is buffered by the walls.

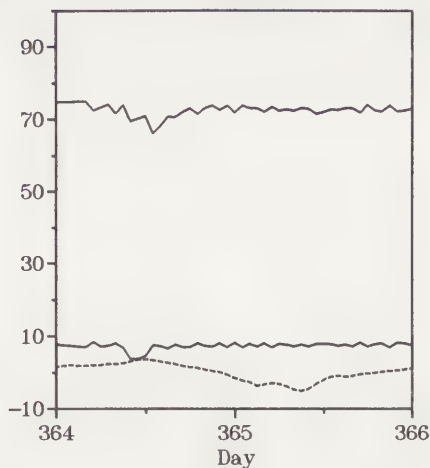


Figure 8. Evidence for RH buffering after a complete filling of the church with fresh air. When the door is opened at 364.4 the dew point of the inside air (lower solid line) drops to the dew point outside (lowest line). When the door is closed the RH (upper solid line) returns rapidly to its earlier value.

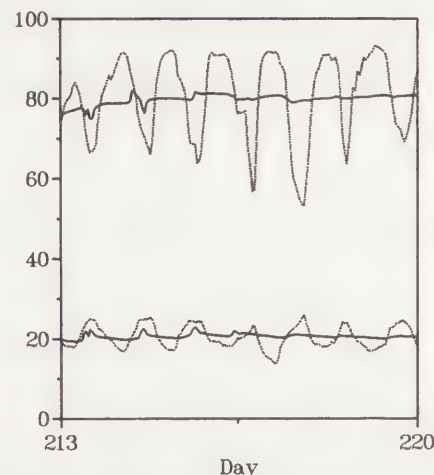


Figure 9. Buffering of the church interior RH over a week in summer. Outside (dotted) and inside RH and temperature are shown.

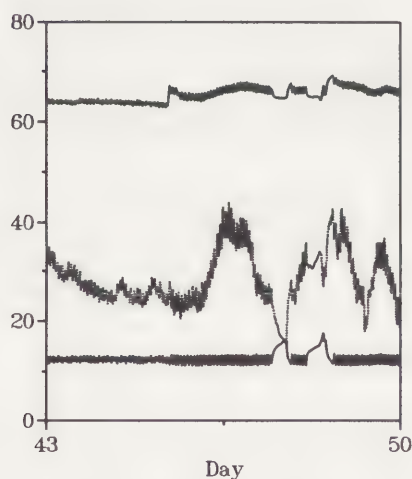


Figure 10. Buffering and natural humidification in winter. RH and temperature inside (solid lines) are shown. The center dotted line is the RH expected inside in the absence of humidification and buffering. It is calculated from the water content of the outside air at the inside temperature.

The wall seems to be performing a double function: evaporation from the lower part and RH buffering higher up. We have tested this theory by measuring the capacity of the wall to absorb water vapour at different heights. To do this we set a damp cloth in an insulated cup and pressed the cup against the wall with a small air gap between cloth and wall (See fig. 11). The temperature difference established between cloth and wall is a measure of the rate of water absorption: evaporation from the cloth withdraws heat from the surroundings (just like a psychrometer's wet bulb), and absorption by the wall releases heat. The rate of water absorption by the wall was zero at 300 mm from the floor but increased up the wall, confirming that the wall is actually functioning in two separate ways.

Fortunately, the remains of the wall paintings, whose preservation provided the impetus for this investigation, are high on the wall, above the zone of evaporation. Indeed, it is possible that the water evaporating from the bottom of the wall is re-absorbed higher up, providing the ideal condition for salts to tend to move away from the painted surface. Unfortunately, this free source of humidification from the rising ground water also draws salts up from the ground, so it cannot be regarded as the ultimate solution. The floor construction, with its capillary-breaking but permeable structure, seems a more elegant solution to humidification of the church, but it does not work fast enough.

Conclusions

A study of the microclimate in Gundsømagle church has revealed that the porous lime plaster of the walls provides a perfect buffering of the relative humidity in the air next to the walls during periods when the church is rapidly warmed for a service, though the temperature difference between wall and air results in a dip in the RH measured in the church. The plaster and the porous limestone walls effectively buffer the inner climate against variation in outside relative humidity, in spite of the 0.25 air changes per hour in the church. The church also humidifies itself in winter, probably through evaporation of water from the saturated lower part of the walls. The wall functions as a source of water in its lower part and as a buffer for relative humidity higher up.

The RH stabilisation provided by porous walls can surely be used in museum architecture. Lightweight concrete's steep absorption isotherm indicates that it will buffer RH even more effectively than the limestone walls described in this article (See fig. 2). Internal walls will buffer perfectly because there will not be a significant temperature difference between wall surface and air.

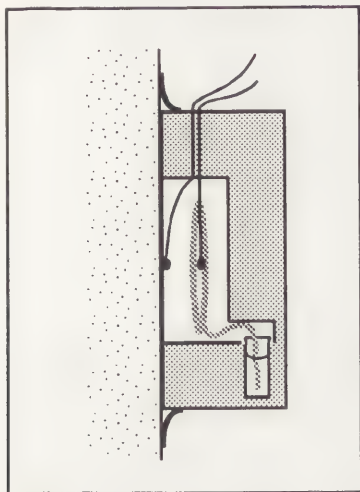


Figure 11. Apparatus used to measure the ability of the wall to absorb water vapour. An insulated chamber is sealed against the wall. In the chamber is a flat bag of wet cotton cloth containing a thermocouple. The cotton is provided with a wick which dips into a small vial of water. A second thermocouple touches the wall surface. The temperature difference, combined with the thermal resistance of the air between cloth and wall, allows measurement of the rate of water absorption by the wall.

Architects could also explore the possibility of free humidification by allowing water vapour to diffuse through porous floors with a rubble layer beneath to break capillary movement and thus prevent the efflorescence of salts on the floor.

All these processes for stabilising RH and for humidifying are most effective when the air exchange rate is fairly slow, about 0.25 air changes per hour. Massive absorbent walls can buffer both the heat and the water vapour from visitors. The only problem is to avoid carbon dioxide poisoning. Ventilation systems that provide the minimum air exchange and an acceptable carbon dioxide concentration are becoming more common in museums. Therefore, there is some scope for a hybrid technology that takes and combines these natural passive processes with cunning technology to make a more economical and maybe more congenial museum design.

Porous outside walls are currently unfashionable in new buildings. The universal trend for buildings in a cool climate is to incorporate an air barrier close to the inner side of the wall, to prevent warm humidified air from moving outwards, cooling and depositing dew within the outer wall, with consequent corrosion and frost damage. Such a barrier is necessary in walls with non-hygroscopic insulation, such as glass fibre and rockwool. We suggest that a re-evaluation of the advantages of homogeneous, hygroscopic, and porous walls might well lead to cheaper and more durable museum buildings.

Acknowledgements

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Abstract

In the mid-1980s, The Getty Conservation Institute (GCI) undertook an extensive environmental research program which included the detection and mitigation of indoor-generated carbonyl pollutants found in museum environments. Carbonyl pollutants were measured in museum galleries, storage areas, display cases, and storage cabinets in locations throughout the United States. The concentrations ranged from less than 0.2 parts per billion (ppb) to nearly 1600 ppb. The highest concentrations were found in areas with little air circulation, such as display cases. Other research focused on evaluation of simple, economical passive sampling devices (PSDs). The best PSD was the GMD Formaldehyde Dosimeter (GMD Systems, Inc., Hendersonville, PA, USA). This dosimeter uses 2,4-dinitrophenylhydrazine to trap airborne carbonyl pollutants which are later extracted and analyzed by liquid chromatography. The sensitivity is less than one ppb for 24 hours exposure. The agreement with conventional active sampling methods was 13%.

Keywords

Pollutants, museum environment, detection, passive monitoring, formaldehyde

Using Passive Sampling Devices to Detect Pollutants in Museum Environments

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Introduction

While the world around us becomes increasingly aware of its effect on the global environment, the conservation community has been alert to potential deleterious effects of the environment surrounding cultural property for several decades. This recognition was precipitated by a number of reported incidents of damage to cultural property while it was on display or in storage (1-12). In many instances, indoor-generated carbonyl compounds, such as formaldehyde and acetic acid have been labeled the culprit. These concerns have led to research projects addressing the detection and mitigation of pollutants in museum environments.

GCI Environmental Research Program

A research program targeting indoor-generated pollutants in the museum environment was established at The Getty Conservation Institute (GCI) in 1986. Several interlocking research areas were investigated, including five major categories.

- Development of analytical methods to detect parts per billion (ppb) levels of pollutants.
- Surveys to assess the problem of carbonyl pollutants in relation to museum type, collection type, museum geographical location and the type of HVAC (heating, ventilation, and air conditioning) system.
- Experiments to understand the relationship between the chemical and physical nature of various materials and damage due to carbonyl pollutant exposure, and thus identify which materials are most susceptible to damage.
- Identification or development of simple, low cost passive sampling devices.
- Investigation of removal or reduction methods for carbonyl pollutants as well as development of general strategies for dealing with carbonyl-based pollution in museum environments.

The focus of this paper is the identification and evaluation of passive monitors to determine ppb levels of pollutants in museum environments. The other branches of the environmental research program will be published elsewhere (13-15). First, the results of the GCI's survey of carbonyl pollutants will be discussed to demonstrate the necessity of passive monitors for pollutants.

Carbonyl pollutants in museum environments

Carbonyl pollutants such as formaldehyde and acetic acid have been suspected to cause damage to objects on display or in storage (16). The survey sought to determine whether or not all collections, regardless of building type or collection type, had high levels of these pollutants. The GCI collected air samples at 17 collecting institutions in North America. Approximately 600 samples were collected from almost 200 sites within these institutions. The air samples were collected from four general areas: galleries, storage areas, storage cabinets, and display cases (17). These data provided typical pollutant levels for formaldehyde, acetaldehyde, formic acid, and acetic acid (12).

Before reviewing the results of the museum survey of indoor-generated airborne carbonyl pollutants, the following reference levels should be considered. In a typical United States home of wood and particle board construction, with no urea-formaldehyde foam insulation, the average concentration of formaldehyde is 30 ppb (18). The outdoor concentration of carbonyl pollutants depends on climate and weather conditions. For Southern California, where the majority

of the participating institutions were located, the outdoor ambient carbonyl concentrations are in the low ppb range (19–21):

formaldehyde	1–29 ppb
acetaldehyde	1–13 ppb
formic acid	1–8 ppb
acetic acid	2–10 ppb

The concentration of formaldehyde in the troposphere is 0.4 ppb, and the concentration of carboxylic acids detected in Arctic air is 0.1 ppb (22, 23).

The survey demonstrated that pollutant problems were specific to building materials and air circulation patterns. While concentrations of carbonyl and carboxylic acid pollutants measured during the air survey ranged from less than the analytical detection limits of 0.2–0.5 ppb to over 1500 ppb, the majority of the sites surveyed had pollutant concentrations less than 20 ppb (See Table 1 and Figure 1). Only display cases and storage cabinets exhibited concentrations greater than 100 ppb. It should be noted that not all display cases and storage concentrations had high levels of pollutants. Concentrations of carbonyl and carboxylic acid pollutants, in general, increased in the following order of the sampling site type:

galleries < storage areas < display cases ≤ storage cabinets

This order reflects the difference in air circulation and air exchange between galleries and display cases.

Table 1. Survey statistics (concentrations presented in ppb): GCI survey of indoor-generated carbonyl pollutants.

	Formaldehyde	Formic acid	Acetaldehyde	Acetic acid
Median	12	6	8	10
Mean	42	14	23	32
Minimum	<0.2	<0.3	<0.2	<0.5
Maximum	1400	290	850	1600

The results of the survey confirmed the presence of carbonyl pollutants in museum environments. Yet it was also discovered that formaldehyde, acetaldehyde, formic acid, and acetic acid are not ubiquitous in museum environments. High levels of carbonyl pollutants could also be correlated to specific building materials used.

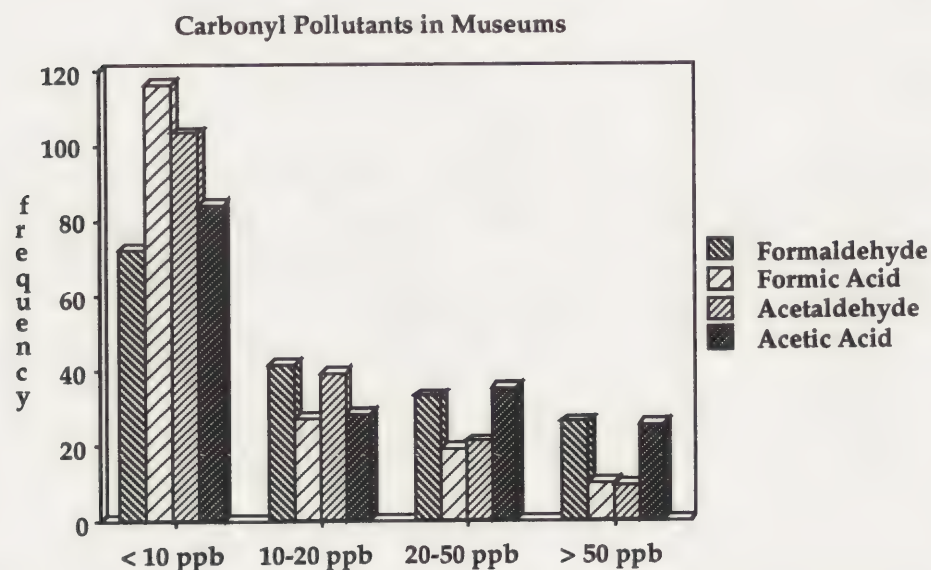


Figure 1. Bar graph chart illustrating the number of sites sampled with concentrations in the various ranges.

Passive monitor project

The methods used in the museum survey of carbonyl pollutants are highly technical and not always available to all institutions (24, 25). The passive monitor project was designed to identify and test passive sampling devices (PSDs) able to detect ppb levels of pollutants. PSDs available on the market for other purposes, such as health hazard monitoring, which could be used or modified for museum pollutant studies were identified. A number of dosimeter-type badges have been developed in response to limits on formaldehyde exposure in the work place. These limits have been set by the Occupational Safety and Health Agency (OSHA) and the American Society of Heating and Air Conditioning Engineers (ASHRAE). With the increasing awareness of the potential health hazards of pollutants, the number of passive dosimeters available for detecting the low levels of pollutants found in the museum environment is increasing. However, the detection limits of these badges can be two orders of magnitude higher than formaldehyde concentrations typically found in museums.

Evaluation of commercial passive monitors

Passive samplers were evaluated based on sensitivity, reproducibility, accuracy and specificity. Detection limits were determined since the median concentration found in the museum survey of carbonyl pollutants ranged from 6–12 ppb. Reproducibility was determined to assess batch variability and to establish the validity of using only one passive sampler at each location to minimize expense. The accuracy of the PSD was determined based on the percent recovery of the passive sampler when exposed to a known concentration. The PSD was then compared to a standardized active sampling method to further corroborate its accuracy. These tests were conducted both in the laboratory and in the field. Because the museum environment consists of many different chemical species, interference studies were performed to identify any substantial positive or negative interferences from other pollutants. Finally, because the results of the GCI's survey of carbonyl pollutants in the museum environment showed that the locations with the highest levels of pollutants were sites with little or no air circulation, such as display cases, the PSDs' effectiveness in a sealed case with no air circulation was evaluated.

Formaldehyde passive monitors

The first phase of the passive monitor project focused on identifying a passive monitor for formaldehyde because this was the most prevalent airborne pollutant detected in the GCI's survey of museum environments. Also, there has been much concern about this pollutant in the conservation community.

The Draeger Formaldehyde Gas Detection tube Model 0,2/a (National Draeger Co.) and the Sensidyne Formaldehyde Detector tube Model 91L (Sensidyne Corp.) were tested. These are low cost, pollutant-specific sorbent tubes with direct-reading color indicators that require active sampling with a hand-held or other pump. A specified number of air strokes are pulled through the tube and the concentration is read at the location of the color change of the sorbent in relation to a scale on the tube. While lower levels of formaldehyde could be detected by increasing the number of strokes through the tube, the number of strokes (40 to 120) required to detect low concentrations of formaldehyde was not practical.

The following commercially-available PSDs were tested; they are based on the diffusion of the pollutant through a barrier membrane (26).

- 3M Formaldehyde Monitor #3720 (3M Co., St. Paul, MN, USA). A bisulfite diffusion badge analyzed by the manufacturer using the chromotropic acid method.
- PF-1 Formaldehyde Monitor (Air Quality Research, Berkeley, CA, USA). A diffusion tube with bisulfite-coated paper analyzed by the manufacturer using the chromotropic acid method.
- Pro-Tek (TM) Formaldehyde Badge Type C-60 (DuPont, Wilmington, DE,

USA). A bisulfite diffusion badge analyzed by designated laboratories using the chromotropic acid method.

- Formaldehyde Dosimeter Badge Series 570 (GMD Systems, Inc., Hendersonville, PA, USA). A diffusion badge with 2,4-dinitrophenyl-hydrazine coated paper, analyzed by the manufacturer or designated laboratories using liquid chromatography with UV detection.
- Air Scan (TM) Formaldehyde Exposure Monitor (Bacharach, Inc., Pittsburgh, PA, USA). A diffusion tube with color development reagent.
- DGA Formaldehyde Monitor (DGA, Ventura, CA, USA). A diffusion badge with 2,4-dinitrophenylhydrazine coated paper, analyzed by the manufacturer or designated laboratories using liquid chromatography with UV detection. (Developed during the research project.)

The majority of the passive monitors tested were designed for much higher levels of formaldehyde than is typically present in museums. The 3M-brand Formaldehyde Monitor 3720 and DuPont's Pro-Tek (TM) badge were not sensitive enough. The detection limits of these badges were two orders of magnitude greater than the concentrations seen in museum galleries. The Air Quality Research Inc.'s PF-1 Formaldehyde Monitor and the Bacharach AirScan (TM) formaldehyde exposure monitors were not good candidates for museum environmental surveys because of reproducibility problems and exposure requirements. The DGA dosimeter was in the designing stage during this research.

Of the seven commercially available passive monitors and detector tubes tested, the GMD 570 Series Formaldehyde Dosimeter badge showed the highest promise for museum applications. This PSD was subjected to the validation tests described previously. It was determined that the detection limit of the GMD 570 Series Formaldehyde Dosimeter badge was 5.6 ppb · hour. Thus, if the badge is exposed for 24 hours, less than a ppb can be detected. The reproducibility of the badge was found to be 95–98%. When the GMD badge was exposed to a known amount of formaldehyde, 99% percent was recovered. The GMD badges were compared to an active sampling method and the ratio of the amount of formaldehyde detected was 1.13; in other words, 13% more formaldehyde was detected on the badge than was detected by active sampling. When the GMD badge was placed in a case with no air circulation, 20% less formaldehyde was detected than in a control case with air circulation. This combined with the 13% gain in observed concentration noted above means that the GMD badge in a sealed case detects 7% less than would be detected with active sampling. It should be noted that the United States Environmental Protection Agency allows a 20–30% difference for comparison of active and passive methods of analysis. The chemical reaction responsible for detection of formaldehyde is very selective; no interferences with typical atmospheric pollutants have been recorded.

The price for 10 GMD badges with pre-paid analysis is \$400 (December 1992 price); if one has access to a laboratory capable of performing the liquid chromatographic analysis, 10 badges may be purchased without analysis for \$100. GMD 570 Series Formaldehyde dosimeter badges are available from GMD System Inc., Old Route 519, Hendersonville, PA 15339, USA (27).

A direct-reading formaldehyde dosimeter requiring no analysis was discovered after the first phase of validation studies. ChemSense, Inc. (Raleigh, NC, USA) distributes direct-reading dosimeters requiring no analysis for a number of atmospheric pollutants. These badges have not yet been tested for use in the museum environment. While they are not as sensitive as the GMD badges described above, they could be used to pre-screen specific areas.

Future research will include the validation of ChemSense direct-reading dosimeters. Passive monitors for outdoor pollutants which are known to infiltrate museum environments such as sulfur dioxide, nitrogen oxides, and ozone will be identified and tested.

Guidelines for using passive monitors

There are a few precautions to follow when using the passive monitors to determine indoor air quality. Most passive sampling devices are stored in a freezer

to extend their shelf life to 6-12 months. Badges can be exposed 8-48 hours. Shorter exposure periods may not be sufficient to detect low levels of pollutant, while longer exposure periods may overexpose the dosimeter badge. The badges should be analyzed as soon as possible after exposure.

Care must be exercised when placing a badge inside a case or cabinet to minimize air exchange with room air. One cannot leisurely place a PSD in a small, closed microenvironment since room air will quickly dilute the air within the case or cabinet. Rather one must open the case minimally and slip the badge into the case or cabinet. Fortunately, the badges are very thin, and this can be done easily.

Conclusion

Passive monitors can be used effectively to monitor the level of formaldehyde within museums. This research showed that the GMD Formaldehyde Dosimeter meets the criteria necessary for use in museums. The badge compared well with active sampling results and is sensitive at the low levels of formaldehyde expected in museum environments.

Acknowledgments

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Abstract

An autonomous indoor/outdoor environmental monitoring station was installed at the Tomb of Nefertari in the Valley of the Queens, Egypt, to record the microclimate of the tomb and to establish a quantitative relation between changes of the microenvironment in the tomb and the presence of visitors.

The temperature in the Tomb of Nefertari remained stable at approximately 29°C year-round, but the relative humidity ranged between 18% in February and 41% in October. The moisture content of the air in the tomb tracked that of the outside, but always remained higher. Emission and dispersion rates of CO₂ and moisture were measured through three controlled experiments conducted in the tomb. The rate of moisture absorption by the tomb immediately following its emission by people entering the tomb was significant in summer but not so significant in winter, since the winter rate of natural ventilation was high.

Keywords

Microenvironment, environmental monitoring, tomb, Tomb of Nefertari

Environmental Monitoring at the Tomb of Nefertari

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Introduction

The causes of deterioration of the wall paintings in the Tomb of Nefertari have been the subject of many investigations (1-4). The report published by UNESCO concluded that three deterioration processes may be affecting the wall paintings in the tomb: seepage of rain water, formation of sodium chloride crystals, and dehydration of the plaster (5).

The crystallization of salt, present in a buried limestone boulder, can be confirmed on many surfaces of the limestone and the paintings. However, the source of water which activates the movement of salt has not been identified. Some investigators have speculated about the following possible sources of the water: rainwater moving through fissures in the bedrock, occasional flooding through the entrance, the water used in the initial preparation of the mud plaster and paint, and environmental moisture generated by visitors.

In the past, several investigators surveyed the microenvironmental condition of the Tomb of Nefertari. However, none of them produced complete year-round data which characterize both the microenvironment of the tomb and the microclimate of the Valley of the Queens. The UNESCO mission found the moisture content of the air outside the tomb to be less than that of the air inside (6). They observed the natural ventilation pattern in the tomb which consisted of cooler outside air entering the tomb at floor level and warmer air leaving the tomb along the top of the entrance staircase. The report, based on measurements taken during January, indicates drying of the wall paintings and dehydration of the plaster taking place during the cold season.

The ICCROM study, which investigated the impact of increased numbers of tourists in the Theban tombs, concluded the climatic impact of visitors to be well below levels considered to be dangerous (7). The report also recommended a continuous monitoring and data collection of the tomb's microenvironment and external environment. However, small yet popular tombs such as the Tombs of Tutankhamen and Sennedjem are constantly visited by ever increasing numbers of tourists. As a result, baseline relative humidities in these tombs have gone up significantly, and microenvironments are created which may be endangering the wall paintings in these tombs. The authors' experience, based on hand-held sensor readings, indicates a less than safe microenvironment (low oxygen content and high carbon dioxide concentration) for visitors in deep or large tombs, where a large volume of visitors is handled with no monitoring of those parameters.

With the increased numbers of tourists in the area since the early 1980s and renewed interest in the Tomb of Nefertari due to the recent publicity on the completion of the wall painting conservation work, pressure on the Egyptian Antiquities Organization to open the tomb to visitors has been high. However, an operational procedure or criteria to ensure the minimum impact of visitors on the microenvironment of the tomb (such as how many visitors, length of visit, and touring pattern) has not yet been established.

The objectives of this study have been to document the microclimate and investigate the impact of visitors on the microenvironment of the Tomb of Nefertari by measuring changes of air temperature, relative humidity, and level of carbon dioxide in the tomb. From this and future environmental monitoring we will try to produce recommendations for the operational procedures and conditions necessary to maintain the safe microenvironment in the tomb and the state of preservation of the wall paintings.

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Orientation, geometry, and materials of the tomb

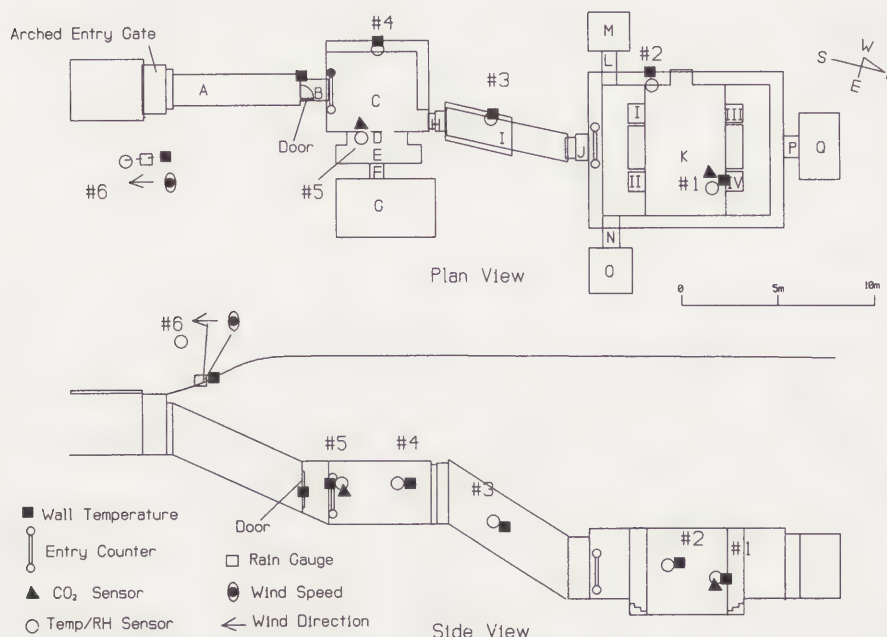
The Tomb of Nefertari is located in the Valley of the Queens, which is approximately 5 km west of the Nile River, at the edge of the hills that form the boundary of the Western Desert of Egypt. This boundary also represents the edge of the Nile Valley which encloses the agricultural strip along the banks of the river. The nearest irrigation canal is approximately 1.5 km west of the tomb and more than 40 meters below the elevation of the tomb.

The tomb is oriented north-south and carved approximately 13 m deep into a large limestone boulder that is buried in the middle of the valley. Investigators reported that the stone is a conglomerate of clayey limestone and water soluble salts which consist of sodium, potassium, calcium, magnesium, sulphate, and chlorides. The reported bulk density of the limestone is 2.1 g/cm^3 with 20.5% open porosity; the water adsorption is about 9.8% of the weight.

The plaster, ranging from 2 to 10 mm in thickness, was laid directly on the stone wall, and the white ground paint layer, which consists of anhydrite with sand grains, α -quartz, and a small amount of calcium carbonate, was applied prior to application of the paint layers. Three types of plasters, clay, gypsum, and lime, were found at various locations in the tomb, and the reported bulk density is approximately 1.6 g/cm^3 .

Figure 1 shows a plan and sectional views of the tomb which is comprised of two major chambers, the funeral chamber (C) and the burial chamber (K), that are connected by a staircase (approximately 7 m long with a 3.3 m drop). A painted steel entry door (1 m x 1.7 m) is attached to a large steel bulkhead on the south wall of the funeral chamber and an approximately 4.5-m long staircase (A) leads to an arched entry gate of the tomb at ground level. The funeral chamber is square (approximately 5.2 m) with a 3.1-m high ceiling. The burial chamber (10.5 x 8.4 m) has three split-level floors that are 2.7 m, 3.4 m, and 2.7 m from the ceiling. The total volume of the tomb was estimated to be 475 m^3 .

Figure 1
Floor Plan (top) and Cross-section (bottom) of the Tomb of Nefertari
and Sensor Locations for Environmental Monitoring



Description of the monitoring system

An autonomous monitoring station was installed at the tomb in August 1991 to record the environment inside and outside of the tomb. The data are periodically downloaded to a personal computer for analysis (8). An air temperature

and relative humidity sensor, ground surface temperature sensor, and rain gauge are installed outside the entrance to the tomb (See fig. 1). Two sets each of the air temperature, relative humidity, and wall surface temperature sensors were positioned in the funeral and burial chambers, and one set was installed in the staircase connecting the two chambers. The air temperature and relative humidity sensors in the tomb were positioned 2-3 cm from the wall surfaces where the surface temperatures were measured. A CO₂ sensor was placed in the funeral and burial chambers, and a photoelectric sensor was also positioned at the low ends of stairways in the two major chambers in order to keep track of the number of visitors into the chambers and their residence time by counting the number of visitors crossing the sensors.

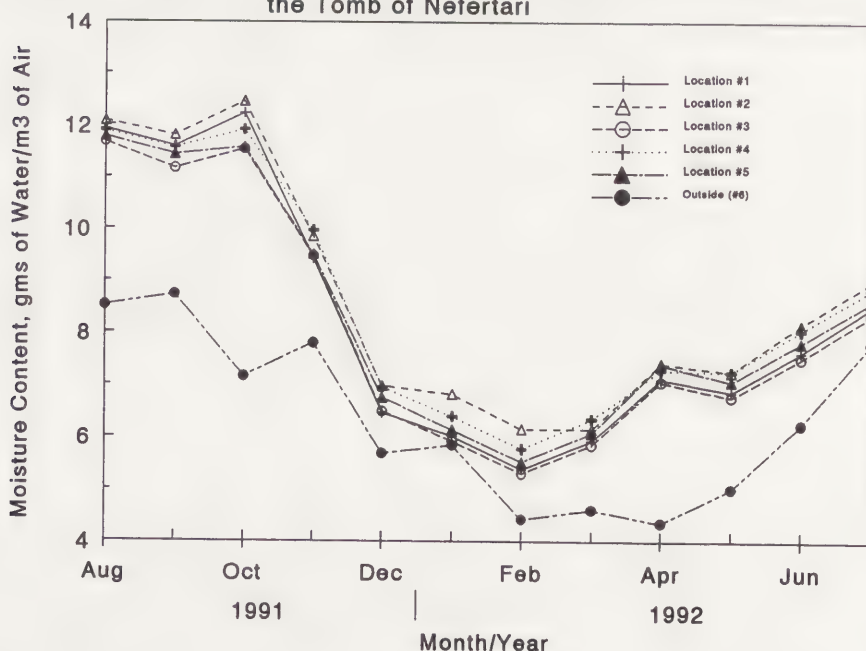
Results of environmental monitoring

Results presented in this report are based on data collected between August 1991 and July 1992. Microclimatic data of the tomb, and results of three controlled experiments conducted in the tomb with visitor groups, are also analyzed.

Climate of the Valley of the Queens

The monthly average of air temperature ranged from 16°C in December, January, and February to 35°C in June outside of the tomb. The extremes of air temperature were 46°C in June and 6°C in December. The average relative humidity ranged from 18% RH in June to 45% RH in December. It dropped down to less than 10% RH in mid-afternoons throughout the year, but it reached above 80% RH only in early mornings in December and January. Although the relative humidity was higher during the winter months than in the summer, the moisture content in the air was 30% to 40% less in winter (See fig. 2).

Figure 2
Monthly Average of Moisture Content of Air Inside and Outside of the Tomb of Nefertari



Microclimate of the Tomb of Nefertari

The air temperatures remained at approximately $29.0 \pm 0.5^\circ\text{C}$ and $28.5 \pm 1^\circ\text{C}$ year-round in the burial and funeral chambers, respectively. The air temperature in the burial chamber was higher than that of the funeral chamber between November and July, and the largest temperature difference, 0.2°C , was recorded in March.

The highest monthly average, 41% RH, was recorded in October in the burial chamber and the lowest, 18% RH, was recorded in February, also in the burial chamber. The annual average was 28% RH and the swing was symmetrical.

Sensors indicated less than 2% variation in RH between the upper and lower chambers throughout the year.

The moisture content of the outside air increased during summer, resulting in an increase of the RH in the tomb (See fig. 2). Although moisture contents of air in the tomb behaved similarly to the outside air for both seasons, they were always somewhat higher. This may be due to the hygroscopic characteristics of the bedrock limestone, mud plaster, paint, salts, and flooring canvas in the tomb, or the moisture contained in the bedrock limestone.

Relative humidity in the burial chamber was extremely stable throughout the month with less than 0.5% RH fluctuation in summer. Therefore, even a brief entry of visitors into the tomb generated a noticeable spike followed by a gradual decay in the relative humidity chart. However, it varied significantly in winter months. The diurnal fluctuation, which was not identifiable in summer months, ranged from 1.0 to 2.5% RH, and the monthly fluctuation was approximately 4% RH in the burial chamber. Peaks of the relative humidity created by entries of visitors into the tomb were sharp and almost like needles in winter compared to the peaks observed in the summer, indicating faster recovery of the tomb in winter months.

Controlled experiments

Three controlled experiments were conducted in the tomb to evaluate changes of the environmental parameters caused by a tour of a typical group of visitors, and the tomb's ability to recover its natural microenvironment following their exit. The experiments were conducted in August, January, and May to identify the effects of seasonal variation.

Twenty to forty local Egyptian male adults entered the tomb and stayed 30 or 60 minutes, then they all exited the tomb at the same time. They stayed in the burial chamber throughout the experiments in order to model the worst possible case in terms of the tomb's microenvironment. During the experiments they walked about the chamber, simulating typical tourists' behavior. The entry door was opened 60 to 120 minutes prior to the experiments and left fully open throughout the experiments. Then it was closed and locked 30 to 60 minutes after the group's exit. Table 1 summarizes the conditions during these experiments.

Table 1. Summary of controlled experiments.

	Experiment no.		
	1	2	3
Number of visitors (adults)	37	21	24
Duration of stay (minutes)	30	60	30
Season (month)	August	January	May
CO ₂ emission rate (ppm/hr/adult)	23	36	59
Moisture emission rate (% RH/hr/adult)	0.34	0.27	0.43
Open-door air exchange rate (m ³ /hr)	24	338	114
Closed-door air exchange rate (m ³ /hr)	8.9	68	27
Average tomb temp/RH (°C/%RH)	29/39	29/21	29/25
Average outdoor temp/RH (°C/%RH)	33/21	15/41	21/15

Rate of changes

Table 1 summarizes results of CO₂ increases measured in the burial chamber during the controlled experiments. The values of 23, 36, and 59 ppm/hour/adult are in good agreement with estimates based on ASHRAE's value (9). If a group of 30 visitors enter the tomb one after another during the site's operational hours (7 am to 4 pm) without a recovery period for the microenvironment, the CO₂ concentration in the tomb will reach 1.1% by the end of the day.

The measured increases of RH range from 0.27 to 0.43% RH/hour/adult, which corresponds to the water emission rate of approximately 50 grams/hour/adult

of water (See table 1). Larger air exchange rates during winter may be the cause of the lowest relative humidity increase.

If the average of the measured values (0.33% RH/hour/adult) is used to estimate a case of the full-visitor load on the tomb, the relative humidity in the tomb will reach 100% RH before the end of the day. However, the hygroscopicity of the tomb takes over as the higher relative humidity environment is created, and the amount of moisture in the air will not reach the saturation value unless the materials in the tomb have already been saturated with the water.

Rates of decay

Immediately following the exit of visitors from the tomb, abrupt drops in CO_2 were recorded in the controlled experiments while the entry way door was left open (See figs. 3, 4). Larger drops were recorded in winter in comparison to those in summer. If the outside air was cooler than that of the tomb, the air flow seemed to have generated a large convective flow in the tomb, and an

Figure 3

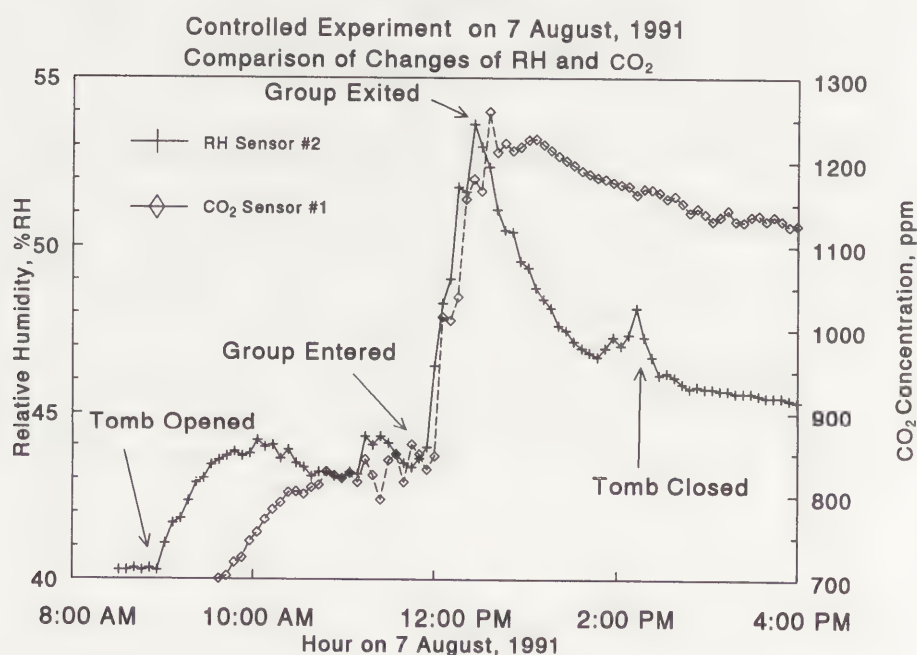
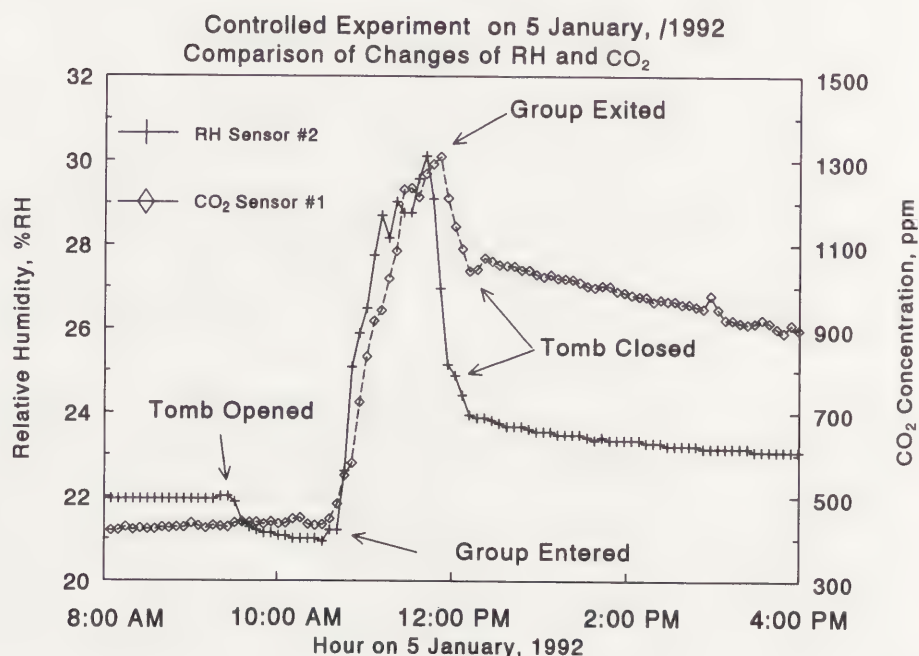


Figure 4



immediate flushing of the tomb with drier outside air started. However, warmer outside air remained near the top of the tomb in summer, creating a stable atmosphere in the tomb.

Air exchange rates of the tomb with its door closed showed significant variations among seasons. The steel entry door allowed a large quantity of air to pass through, especially during winter. Not only is the steel bulkhead loosely fitted to the entryway passage, but also 20 6-cm diameter air holes are drilled through the bulkhead, half of which are left open for air to pass through.

The initial decay of relative humidity was much faster than that of CO_2 as shown in Figures 3 and 4 for summer and winter, respectively. However, the relative humidity decay rates approached the decay rates of CO_2 in 4-5 days during summer and within 1-2 days in winter. Then they reached rates slightly less than those of the CO_2 (See Figures 5, 6).

The moisture in the tomb left by visitors was quickly absorbed by the hygroscopic materials of the tomb, and the excess moisture in the air was then transported

Figure 5

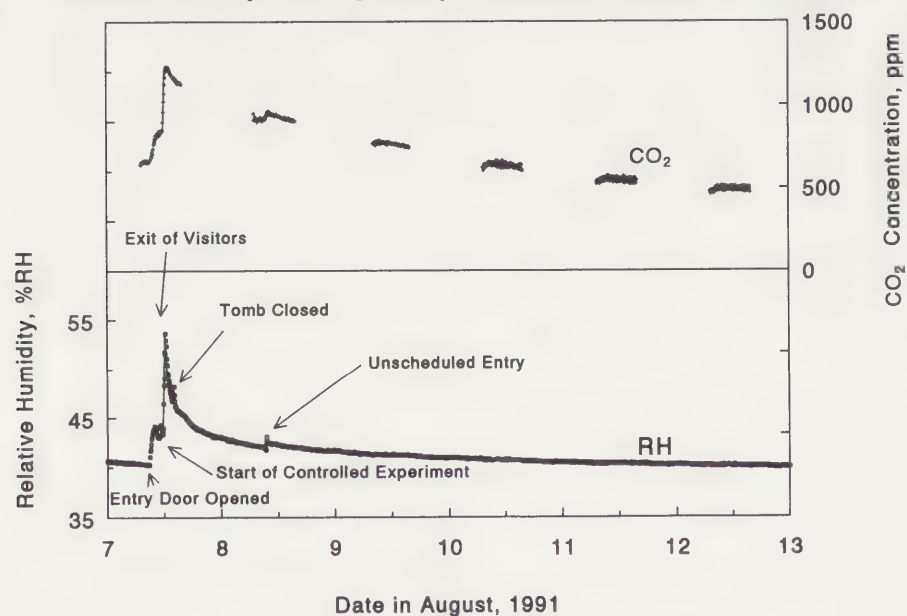
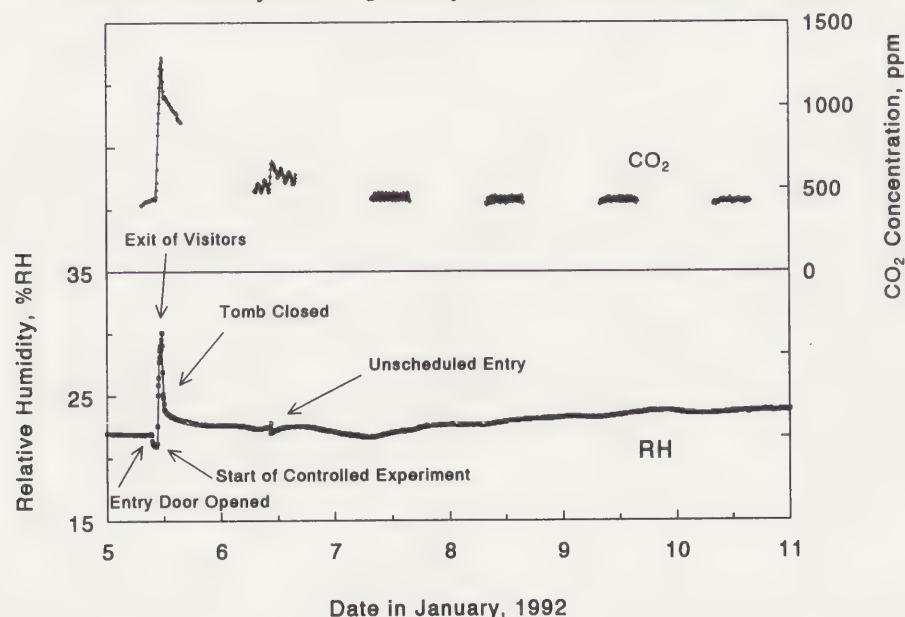
Relative Humidity and CO_2 Decays in the Burial Chamber in Summer

Figure 6

Relative Humidity and CO_2 Decays in the Burial Chamber in Winter

to the outside of the tomb by natural ventilation. The hygroscopic materials started to release the moisture as relative humidity in the chambers decreased. They continued to release excess moisture until it reached equilibrium with the microenvironment of the tomb.

During August, 47% of the moisture generated in the burial chamber remained in the tomb even three days after the event, and it took 12 days before the effect reduces to 5%. However, in January it decreased to 30% in just one day and down to 5% in less than two and a half days.

Conclusions and future work

The temperature in the Tomb of Nefertari remained stable at approximately 29°C year-round, but the relative humidity ranged between 18% in February and 41% in October. The moisture content of the air in the tomb tracked that of the outside, but always remained higher. Although the microenvironment of the tomb was stable in the summer months, it responded quickly to changes of the outdoor environment in the winter months. This was due to a large ventilation rate, which is thermally driven, in winter.

Emission rates of CO₂ (39 ppm/hour/adult) and moisture (0.33% RH/hour/adult) were measured through three controlled experiments conducted in the tomb in August, January, and May. A high rate of natural ventilation was observed with the entry door both opened and closed during winter, but reduced to one-eighth of that in summer. The rate of moisture absorption by the tomb immediately following its emission was significant in summer but not so significant in winter, since the rate of natural ventilation was high. The natural ventilation diluted the moisture in the air and then desorbed the moisture from the tomb. Therefore, long-term decay rates of relative humidity inside the tomb were very similar to those of the air exchange rates, indicating the natural ventilation to be the moisture-removing mechanism of the tomb.

Visitation of the tomb in summer months should be strictly limited, since the baseline RH is high and natural ventilation is at a minimum. Limited numbers of visitors may be allowed in winter if the microenvironment is carefully monitored.

Information on the microenvironment of the Tomb of Nefertari was gained through one year of continuous monitoring. However, the data presented provides only partial understanding of the microclimate and the dynamics of the microenvironment to any disturbance. In order to fill the gap which was identified during the preparation of this report, the following study will be conducted during the next year of monitoring:

- The year-round condition of the undisturbed or least disturbed tomb will be monitored.
- Controlled experiments, similar to the ones described above, will be performed throughout the year to further evaluate rates of natural ventilation in various seasons.
- An attempt will be made to develop a simple mathematical model to simulate effects on the microenvironment of the tomb by the following factors: various visitor patterns, including the number of visitors, duration of individual tours, recovery periods between tours, and periods of operation.
- Monitoring of the microclimate of the sealed tomb will be attempted.

Acknowledgments

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Abstract

Relative humidity specifications for museums became very stringent during the 1960s and 1970s, without detailed explanation. The Canadian Conservation Institute has reviewed the relevant data in order to answer common cost/benefit questions, not just stipulate "correct" RH. Mechanical, biological, and chemical deterioration all rise sharply beyond 75% RH, and increase significantly for every increment to 100% RH. Fracture in rigid, constrained organic artifacts, given a relaxed state at some middle RH, becomes probable in one cycle only for a drop of -25% to -50% RH. Fatigue models imply that each reduction of fluctuations to one half of this critical value will reduce deterioration per cycle to 0.01%–0.00001%. Many flexible or sliding assemblies are immune since constraint is missing.

Keywords

Relative humidity, museum environment, standards, specifications

Relative Humidity: A Discussion of Correct/Incorrect Values

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Introduction

The very words "damp" and "dry" contain an ancient understanding of relative humidity (RH) that has proven very difficult to specify. Despite this, bureaucrats and designers needed a single "correct" relative humidity, and conservation obliged. The ensuing questions were inevitable: Why this number, and how important are deviations?

History of relative humidity specifications

By the turn of the last century, Rathgen had dismissed bacteria as the explanation of bronze disease and shown that an airtight case with desiccant would cure unstable patina (1). As to organic materials, Church stated that "if a stream of warm and dry air enters a gallery . . . the canvases, frames, and panels become altered in shape and size each day. . . Thus the colored films . . . are submitted to an injurious strain, which may end . . . in a multitude of minute fissures, and the final flaking off of portions of the paint." (2)

In 1929, the National Gallery (London) instigated research on panel paintings. The wood scientists demonstrated damage with large RH fluctuations, but did not recommend a "correct" RH (3). Instead, they looked for the best vapour barrier for the back, just as Buck did in the United States. It was left to the building engineer, MacIntyre, to propose a value: 55%RH–60%RH, based on London's climate and on feasibility. He noted an advantage of low RH (reduced pigment fading) and wondered what its effect might be on paper and canvas. He concluded that without this knowledge "optimum conditions for any particular class of paintings must be more or less arbitrary." Finally, he foretold that "the maintenance of the plant and control gear cannot be left to the ordinary attendant." (4)

During the 1930s, the National Gallery determined that their annual average for the moisture content of wood was 11%, so deduced an average RH of 58% (5). Thus, the feasibility argument and the annual average argument had converged (for pre-war London). This became the setpoint for wartime storage in a slate quarry, during which normal panel damage disappeared. After the war, the National Gallery installed control systems, 20 years after MacIntyre's proposal.

By the 1960s and 1970s, designers worldwide demanded specifications by which to build. The familiar numbers, 50% RH or 55% RH, emerged from many experts, but actual knowledge about humidity had not changed in 100 years. What about small fluctuations? As before, feasibility became the determinant that determined fluctuations of $\pm 2\%$, $\pm 3\%$, or $\pm 5\%$, depending on one's experience and one's concept of measurement (much of which was naive).

The numbers became standards: Class A, Class I, ideal! Museum users assumed that the values were scientific, based on a significant minimum in deterioration. The originators knew 50% RH emphasized mechanical phenomena and neglected chemical phenomena; they knew that it was a nice round number and that the specified fluctuations were not derived from artifact needs, but in the museum world at large, non-conformity became transgression.

The "best available" feasibility argument assumed that even if it did insignificant good, it could do no harm. Unfortunately, the mechanical systems were unorthodox, expensive to build and to maintain. Reliability was compromised. In cold climates, humidification was wrecking buildings. Historic walls were gutted in dubious attempts to install vapour barriers and machinery. Deviations from the specifications consumed inordinate amounts of staff time in detection and

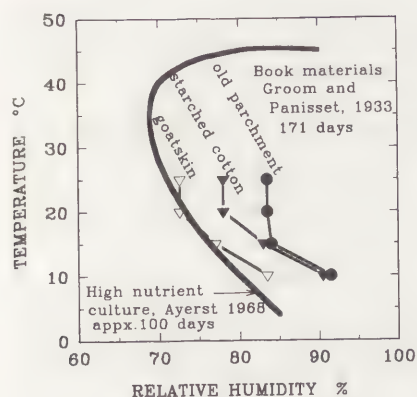


Figure 1. Lowest values of RH that will support mould growth (book study: one species; culture study: many species.)

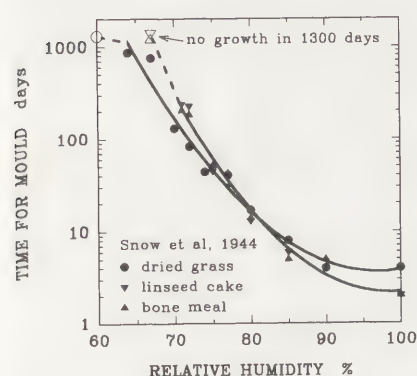


Figure 2. Time required for mould to develop on some high nutrient materials (first appearance of mycelium, many species).

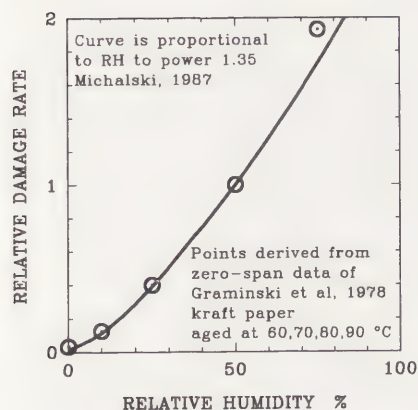


Figure 3. Effect of RH on rate of loss of strength in paper fibers.

response. And what of the artifact loans denied, grants determined, and new buildings justified by the magic numbers? What, exactly, was it all in aid of?

Deterioration by incorrect relative humidity

For practical purposes, incorrect relative humidity can be divided into four types: 1) damp; 2) RH above or below a critical value; 3) RH above 0%; and 4) RH fluctuations.

Deterioration by damp

In 1933, Groom and Panisset published the one accurate study of RH effect on mould growth in museum materials (29 book materials, old and new) (6). The samples with the lowest minimum RH for growth amongst each of parchments, cellulose, and leathers are shown in Figure 1. In 1968, Ayerst reviewed 40 years of industrial data (7). Figure 1 shows his outer limit for growth of a wide variety of common species on a highly nutritive substrate. A few species have been shown to grow (very slowly) in the range 60–65% RH (8,9). It is incorrect to extrapolate plots like Figure 1 from one EMC, as Nyuksha did, thereby concluding paper could mould at 30% RH (10). Within a single material, however, moisture content is the accurate parameter when comparing samples at different states of sorption hysteresis. In leather, mould that develops at 78% RH following a wet cycle will not develop after a dry cycle until 90% RH (13.5% EMC for both, 300 day test) (11). Within these limits, RH has a profound, practical effect: speed (See fig. 2). Speed varies logarithmically between days at 90% RH and years at 65% RH (12).

Overall, several days of damp cause mould in leather and "dirty" (nutrient rich) artifacts only if RH exceeds 80%. Clean paper, paint, and textiles need over 90% RH. In the range of 90%–75% RH, a 10% RH reduction controls mould growth as much as dropping the temperature from 30 to 10°C. A conservative limit for no mould, ever, on anything, would be to stay below 60% RH, but the practical danger for most situations begins above 75% RH. In either case, an excursion to 90% RH is tolerable (in terms of mould) as long as it does not exceed a day or two.

The moisture diffusion coefficient of organic materials increases with moisture content. Capillary wicking of condensate penetrates faster than vapour. On the other hand, drying solids form a low permeability skin which slows drying. Thus, a 1-cm thick wood board takes one hour to get waterlogged and 10 to dry (13). I believe this asymmetry explains the traditional insistence on openings in the backing boards of paintings. A closed but permeable board would push the back of the painting to an RH higher than the ambient average. After a damp night in an unheated building, only convection through large openings would dry the painting by late afternoon. With heated galleries, polluted air, and impermeable boards, such ventilation becomes counter-productive.

Deterioration by RH above or below a critical RH

Waller has recently compiled dozens of critical values available for RH-sensitive minerals, some of which apply to the patina on metals (14). This precision leads away from a generalized "safe" RH towards an emphasis on particular conditions for particular artifacts (and decontamination treatments). Despite this, experience demands that a generalized region of rapid inorganic deterioration must be identified for the non-specialist: damp. Both metal surfaces and particulate dirt show the classic sigmoidal adsorption curve that bends sharply upwards at 75% RH, as the adsorbed water changes from 2-3 molecules to a liquid film (15). Besides, the most ubiquitous salt contaminant, NaCl, deliquesces at 76% RH.

Deterioration by RH above 0%

I re-analyzed some of the data from the monumental study of paper by Graminski, Parks and Toth and fitted a two stage linear decay to the fiber strength (zero span data) (16,17). The rate of strength loss fits a simple power law of RH, exponent 1.35 (See fig. 3). The yellowing data fits a similar power law.

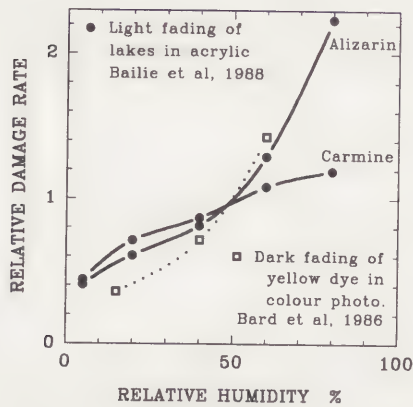


Figure 4. Influence of RH on fading of some colourants.

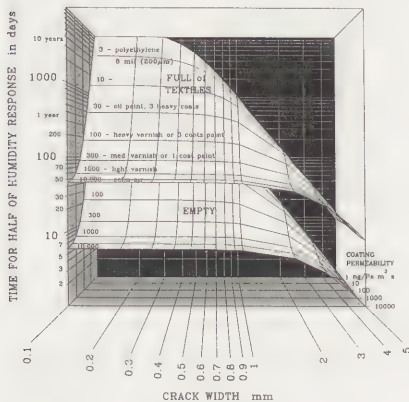


Figure 5. 3-D chart of moisture half-time of a chest of drawers, with and without textile contents, as a function of various coatings or wrappings, and various cracks at top and bottom for natural convection.

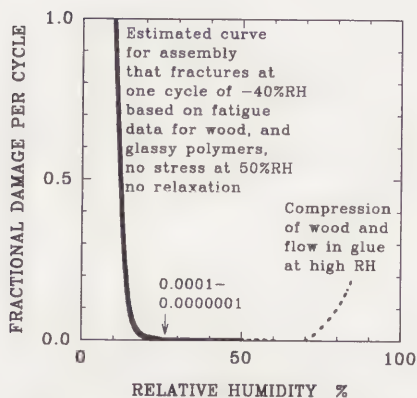


Figure 6. Estimated shape of curve for mechanical damage as a function of RH fluctuation from some middle value.

The "zero" RH data point for both can be fitted to the power law at 2-3% RH, or considered an independent slow mechanism. (This is academic, since practical RH control will not go below 2-3% RH.)

The dark and light fading of dyes is much less profoundly influenced by RH (See fig. 4) (18,19).

Deterioration by RH fluctuation

For most organic materials, the EMC/RH curve is sigmoidal, with knees near 25% RH and 75% RH. For wood, the absorption coefficient almost doubles from 0.14 in the range 40%-50% RH to 0.25 at 0%-10% RH and triples by 85% RH (20). Thus, fluctuations of $\pm 20\%$ RH cause less than half the dimensional change of $\pm 40\%$ RH.

Fluctuations under one hour do not affect most museum objects. The outer layers of bare wood may have shorter response times than the whole; on the other hand, furniture with typical coatings does respond fairly uniformly throughout its thickness. Various charts have been produced at the Canadian Conservation Institute (CCI) to help estimation of response times. Figure 5 demonstrates the contributions of air leakage, wood coating, and textile buffering on the response of a chest of drawers. It shows that it is risky to display furniture empty and open, as compared to normal usage.

The most stressful fluctuations are longer than the response time, but shorter than the stress relaxation time. Glue, gesso, wood, paint, and varnish have very different relaxation times, and all are strongly increased by low RH and low temperature (21). I have modelled the cracking of gilding and suggest that low RH causes more cracking than high RH because the relaxation time of the gesso changes from days to months (22).

Animal glue is the most common historical adhesive, and it changes from a strong, glassy material at low RH to a weak, rubbery material above 80% RH. Glued veneer can either let go completely (buckle) at high RH or more subtly, slide to a new position and readhere there as the humidity drops. CCI has demonstrated this pre-stressing effect in veneer/frame assemblies made at 50% RH: a low humidity cycle caused no failure, unless it was preceded by a 90% RH cycle that caused slippage (23).

Stresses below the critical value necessary to fracture an assembly in one cycle can still cause incremental growth of cracks from microscopic flaws inherent in real materials. The resultant "fatigue" lifetimes depend logarithmically on stress reduction. They reach 1-10 million cycles between one half the stress in tough polymers (wood, skin) and one fifth the stress in brittle polymers (glue, gesso, paint, bone, for cycles shorter than relaxation times). If this fatigue dependence on stress/strain is transformed to a dependence on RH fluctuation, then a curve like Figure 6 emerges: a wide forgiving region and a sudden, steep climb to danger. Indeed, given that about $\pm 25\%$ RH daily was most common historically (given a house free of damp) the estimate for brittle materials conforms to the observation that paintings developed full craquelure in about a century (30,000 daily cycles) whereas areas of the painting protected from daily fluctuation by the stretcher bar often remained free of all but one or two cracks (100 seasonal cycles). Moderately vulnerable assemblies in wood (tough material) suffered very little in these conditions.

Aside from all of the above considerations about material response, humidity fluctuation damage depends greatly on the geometry of assembly. Constrained textiles show very little tension change between 75% RH and 0% RH, because of crimp in the yarns. Textiles can shrink dangerously in the region 75%-100% RH, especially above 90% RH.

Knowledgeable joinery is designed for movement: panels float, dovetails loosen and retighten. Most antique tabletops in Canada pass through wide humidity fluctuations without cracking, though many show permanent plastic compression ("shrinkage"). The attachment to the side rails underneath generally consists of a few large screws that slip or bend before the top breaks. Any short wood

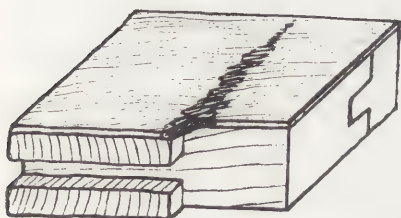


Figure 7. Common high vulnerability assembly: veneer over joint that has failed. The veneer shears as shown.

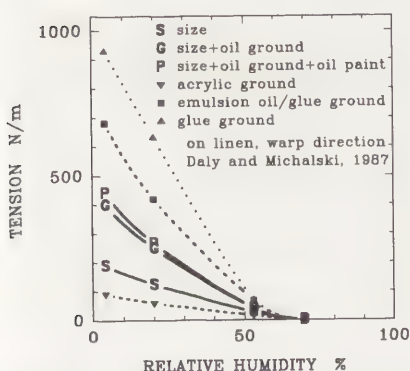


Figure 8. Effect of 0-70% RH on the tension in paintings. At 70-100% RH, the linen dominates and may rise in tension ("shrinker").

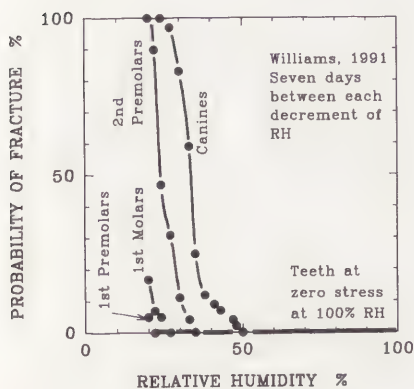


Figure 9. Fracture of fresh teeth in a natural history collection as humidity drops.

blocks that were glued have generally let go. These were purposeful "safety valves."

Radial shrinkage of most woods for a drop of -25% RH is 0.5%, for -40% RH about 0.9% (24). Mechanical studies show wide boards (Douglas fir) can be stretched only 0.2% before cracking if stressed over one day, but stretches 0.5% over one week and 0.8% over two months (25). Thus, furniture that typically takes a week to reach 90% of response to a humidity change will face high risk only for drops in the range -25% RH to -40% RH. No one knows how much further wood can relax, but creep-rupture studies currently include plans for 10-year experiments. Creep will also be higher in boards or veneers held uniformly over their whole face, because the worst flaw no longer has access to all the elastic energy of the stressed assembly. Thus, veneers and lap joints are less vulnerable to cracking than panels jammed in their rebates.

The most common, highly vulnerable assembly in furniture is veneer (or coating) over a joint. As long as the joint remains solid, the veneer is only moderately vulnerable, but if the glued joint has loosened, then the veneer is sheared when the cross grain piece shrinks (See fig. 7).

I have reviewed the data on RH effects on painting materials and glue grounds elsewhere (26,27). Further valuable work by Mecklenburg has appeared (28,29). Although tension change at low humidity has become fairly predictable, fracture has not (See fig. 8). Calculation and experiment to-date indicate that these assemblies require a humidity drop of -50% RH before they reach a high probability of cracking when new. Ageing of the coatings, UV exposure, reduction in adhesion, cracks, and delamination from other causes will all reduce this value, probably to about -25% RH.

Some materials are already under tension at middle RH, e.g. plywood lamina, over keyed-out paintings, paints and gesso with curing stress. Large timbers and whole teeth are prestressed at middle RH because they have circular grain and formed at 100% RH. Figure 9 shows the probability of fracture of fresh teeth as a function of decreasing RH, from Williams (30). As with wood, a hollow center (molars) very much reduces constraint as compared to solid centers (canines). Such pre-stressing will relax out eventually in uncrosslinked constituents (e.g., lignin, collagen, cellulose), but it may take decades.

Furniture and polychrome survived fairly well in Europe prior to modern heating. The problem was damp, not dryness. Sustained drops from the annual average rarely exceeded -25% RH, except next to the fire. Then, heating technology improved. Objects were shipped to cold North America. Drops of -40% RH could occur daily. Still, heating went down at night, the upstairs was cold most of the time, and room furnishings could buffer daily fluctuations. Then, central and overnight heating developed. Drops of -40% RH became sustained winter extremes. Many traditional assemblies that had survived intact until now, cracked and delaminated. This all confirms that between -25% to -40% RH drop, the probability of single cycle damage jumps in traditional assemblies. It also shows the danger in sustaining the fluctuation for the week or more necessary for 90% of response in furniture. I have carefully monitored several pieces of 19th- and early 20th-century furniture, tools, books, and textiles, submitted to 10 winters near 10% RH, some for the first time below about 25% RH. The results confirm two important facts: vulnerable designs considered acceptable practice during their day can survive about -25% RH drop, but not -40% RH drop; on the other hand, many assemblies accommodate -40% RH without problems.

Conclusions

A middle RH makes sense for the rigid organic materials that inspired it, especially paintings. The definition of "small" fluctuations, still problematic, depends on mechanical fatigue. Fatigue shows a powerful decrease in damage per cycle as the fluctuation diminishes below the critical value. How to know the critical fluctuation? Two strategies occur: proofed value and analysis. Proofed value is the largest fluctuation to which the artifact has responded in the past,

so any single cycle damage has occurred for this value. If the material properties have not weakened much (e.g., centuries for wood, decades for paint not exposed to UV), then collections that have seen fluctuations of $\pm 20\%$ to $\pm 40\%$ RH must experience minute or zero damage at one half of this.

Artifacts from more benign conditions, as well as recently keyed-out paintings, have lower proofed values. Strong consolidation of fully developed cracks that used to open and close harmlessly will reset the critical value to less than the proofed value (e.g., old checks, sheared veneer). On the other hand, consolidation of partial cracks due to other effects (e.g., bending, damp, ultraviolet light, leaching, loss of adhesion) will reduce vulnerability to damage.

Analysis, though not precise, can set priorities. Well-designed joinery has only low to moderate vulnerability; incompetent designs are highly vulnerable. In historic houses, it would be possible to estimate which furniture was likely to suffer and which was not. Experiments for such an "atlas" of design vulnerability are planned at CCI.

The extension of the small fluctuation criterion to all artifacts has no merit except convenience. Drops of -40% RH do not constitute an emergency for loose skins, fur, textiles, costumes, metals, botanical specimens, or most archival material. In fact, it is a period of reduced decay.

For libraries and archives holding acidic paper bound with paper products, specifying 50% RH in cold climates simply doubled the rate of chemical decay, by eliminating the winter lull. Leather bindings on non-acidic paper are indeed a mechanical issue, but they can only be considered low to moderately vulnerable assemblies. Brittle inks on parchment are highly vulnerable.

For collections dominated by rigid organic materials (wood and paint), we must accept that the data supports common sense, not magic numbers. Safe RH is a broad valley, like that shown in Figure 6. The slopes may be defined by science, but locating them still depends on experience. Overall, high risk begins outside the range 25%–75% RH. Slight mechanical damage will accumulate on highly vulnerable assemblies at $\pm 20\%$ RH but this is virtually eliminated by $\pm 10\%$ RH in wood, $\pm 5\%$ RH in paint. Middle RH can be the local mean, or international norm. If tight control sacrifices long-term reliability of the 25%–75% RH limits, or other issues like fire and pests, I believe it is counter-productive to the total well-being of most collections.

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Abstract

The environment in the Sainsbury wing of the National Gallery is controlled to give an relative humidity between 50 and 60%, with mean winter and summer temperatures of 19 and 23°C, respectively. Chemical filtration reduces the level of NO₂ and SO₂ in the indoor air to less than 10 µg m⁻³. Natural and artificial light are filtered to reduce the ultraviolet content to less than 10 µW lumen⁻¹. The daylight levels are adjusted with louvres to ensure that the annual exposure is less than 650k lux-h. The temperature, relative humidity, and light levels are monitored by a computerized logging system.

Keywords

Environmental control, air pollution, lighting, ultraviolet, monitoring, computer, National Gallery (London)

The Environment and Lighting in the Sainsbury Wing of the National Gallery

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Introduction

The Sainsbury wing of the National Gallery was opened to the public in July 1991. The daylit, top floor rooms house the Gallery's collection of early Renaissance Italian and northern European paintings. These are mainly on panel and include some of the most fragile objects in the collection. It was considered of vital importance that the conditions in the new galleries be stable before the paintings were transferred from the existing building. The sections which follow describe some aspects of the testing scheme that was instigated at the Gallery during 1988–1991 and the ongoing monitoring of environmental conditions.

Conservation criteria

In common with many other galleries and museums, the National Gallery attempts to maintain the environmental conditions specified for a Class 1 museum in the *The Museum Environment* (1). For climate, these figures have been adapted to provide the following specifications: for winter, relative humidity (RH) 55 ± 5%, temperature 19 ± 1°C; for summer, RH 55 ± 5%, temperature 23 ± 1°C. The difference between winter and summer temperatures acknowledges the need for fuel economy, while providing conditions that are comfortable for the visitors and the security staff in each room. The set-point temperature of the rooms is adjusted slowly during the spring and autumn.

The Class 1 museum specification calls for the removal of particulates and gaseous pollutants from the air in the exhibition areas. The levels for gaseous pollutants that were specified for the Sainsbury wing were sulphur dioxide and nitrogen dioxide concentrations less than 10 µg m⁻³, and ozone concentration less than 2 µg m⁻³.

The paintings to be housed in the new wing, with a very few exceptions, fall into the category "moderately sensitive to light." The specified maximum light level for such exhibits is 200 lux or an annual exposure of less than 650k lux-h. The only major departure from Class 1 museum specification was in the matter of ultraviolet radiation. In the light of previous research, the maximum permissible ultraviolet content was reduced from 75 to 10 µW lumen⁻¹ (2).

The specification of conservation criteria formed an intimate part of the architectural brief for the new wing and thus influenced the decisions of the architects, lighting consultant, and services engineers.

Monitoring climate in the existing building

For many years, the National Gallery has operated a centralized system for environmental monitoring (3, 4). Most rooms in the Gallery contain temperature and relative humidity sensors which record the conditions and provide control signals for air-conditioning plant. The computerized record of environmental conditions was consulted to ascertain the prevailing temperature and RH to which the Renaissance collection had been exposed over the past decade.

The records for the air-conditioned rooms in the west wing and northern extension, which housed the relevant part of the collection for many years, indicated that these paintings had been hung in areas in which the RH had been maintained between 45 and 60% for the great majority of the last decade and which had not varied greatly over short periods. The paintings had not suffered from exposure to high humidity, but had, on some occasions, been subjected to

short periods of RH as low as 40%, the long-term effects of which may not yet be apparent.

Air-conditioning design

Details of the air-conditioning system have been published elsewhere (5, 6). For the purpose of air-conditioning, the building was divided into two zones. The first comprises the main floor galleries, the temporary exhibition galleries, and the packing and storage areas. These are provided with full air-conditioning with chemical filtration, and the temperature and RH are controlled within the tight limits set out above. The large number of visitors, over four million each year, precluded consideration of a more passive environmental control system in the galleries. The second area comprises the other public spaces, including the restaurant, lecture theatre, and staircases. These areas provide a buffer zone between the galleries and the outside, and their environment is controlled less stringently.

The plant for the gallery areas consists of two independent, variable air volume (VAV) air-handling units with steam humidification. Air leaves the plant room with a RH of 80% and a temperature of 12 to 18°C depending on the time of year. The final temperature and RH of the supplied air are controlled by VAV boxes fitted with electric heaters, which are located at the inlet to each individual space. The operation of all aspects of environmental control is regulated by a building management system (BMS).

Each conditioned space is equipped with a set of three temperature and three relative humidity sensors which are connected to the BMS and operate on a "triple redundancy" principal; the readings from the two sensors in closest agreement are averaged and used as a control signal while the reading from the third sensor is used as a calibration check.

Testing the performance of the air-conditioning system

Before any of the paintings were moved, three phases of testing were undertaken to ensure that the conditions in the new wing were within the specification. First, the installation and function of the individual components of environmental control system were checked. The relative humidity and temperature sensors were checked against calibrated instruments. The data for temperature and RH recorded by the BMS were compared with readings made in the galleries. The ability of the BMS to monitor the hot and chilled water supplies and to operate the elements of the air-conditioning system was checked.

In a second phase, the environmental control system was tuned to ensure that the component parts operated in concert under the control of the BMS and that the complete system was able to cope with adverse conditions. Data logged by the BMS were compared with recordings made in the gallery spaces using portable logging equipment. Good agreement was obtained between the two records.

The ability of the air-conditioning system to respond to extremes in temperature and RH was assessed by simulating these conditions in the galleries. In a series of loading tests, the maximum occupancy of a room was simulated using 100W lamps to represent the sensible heat of each visitor; kettles, controlled by variable transformers, were used to provide an appropriate evaporation rate. During these tests, the temperature remained at $19 \pm 1^\circ\text{C}$ and the RH at $55 \pm 3\%$. The signals from the BMS to various parts of the air-conditioning system were monitored to assess the performance of the controls. As a result of this experiment, a small modification was made to the control system.

Finally, after all these checks had been made the rooms were left for a six-week period of "stable running" to ensure that the environmental systems under the control of the BMS were capable of maintaining a stable climate over this time. The temperature and RH were monitored throughout the period using the BMS logging system. Only at the successful conclusion of these tests were the paintings moved from the existing building. Figures 1 and 2 show the weekly records for a representative gallery before and during the test period.

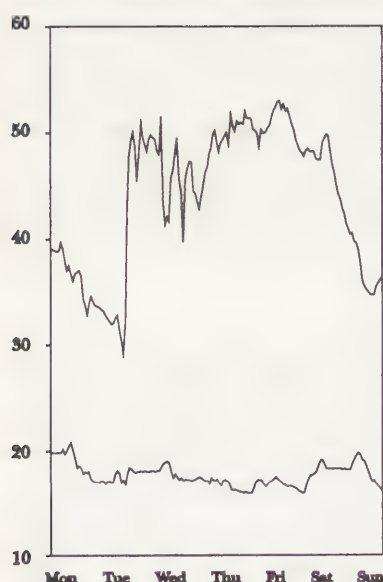


Figure 1. Temperature ($^\circ\text{C}$) and RH (%) in one of the Sainsbury wing galleries for one week prior to the testing the air-conditioning system.

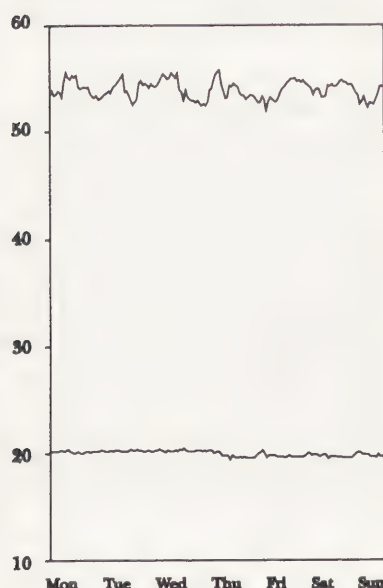


Figure 2. Temperature ($^\circ\text{C}$) and RH (%) in one of the Sainsbury wing galleries for one week during the period of "stable running."

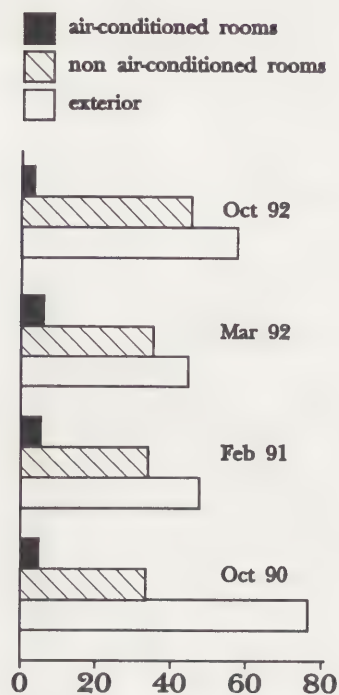


Figure 3. Average nitrogen dioxide concentrations ($\mu\text{g m}^{-3}$) in rooms in the existing building.

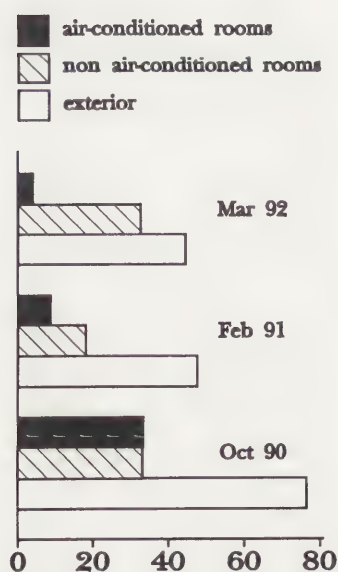


Figure 4. Average nitrogen dioxide concentrations ($\mu\text{g m}^{-3}$) in rooms in the Sainsbury wing before and after the commissioning of the air-conditioning system.

Pollutants levels in the existing building

In central London, one of the principal gaseous pollutants is nitrogen dioxide, NO_2 . First, we conducted a survey of NO_2 levels in the existing building using a passive sampling technique similar to that used previously at the Tate Gallery (7). Passive samplers offer a low-cost method of monitoring a number of locations simultaneously without the need for a power supply. Their main disadvantage is that they give a time-averaged or cumulative level for the pollutant gas.

The diffusion tube samplers used were developed by the United Kingdom Atomic Energy Authority (8). While one tube was left unopened and stored in a refrigerator to act as a control, the remaining tubes were secured in a vertical position and the lower cap removed to commence sampling. NO_2 that diffused into the tube was absorbed on a coated stainless steel mesh. After approximately two weeks, the cap was replaced and the tubes returned to the supplier for analysis.

Samplers were placed outside the Gallery, in air-conditioned rooms and in rooms with no chemical filtration. The results are summarized in Figure 3 and show exterior NO_2 levels of $44\text{--}76 \mu\text{g m}^{-3}$. These agree with a UK Department of the Environment study which reported average NO_2 levels for central London of $53\text{--}103 \mu\text{g m}^{-3}$ over the period 1973 to 1987 (9). In those rooms that are not air-conditioned, the NO_2 level varied between 40 and 80% of the exterior level, with a maximum level of $45 \mu\text{g m}^{-3}$. In contrast, the NO_2 levels in galleries with air-conditioning (all of which have chemical filtration) ranged from $0.9 \mu\text{g m}^{-3}$ to $10.3 \mu\text{g m}^{-3}$.

Pollutant levels in the Sainsbury wing

The low levels of pollutant gases specified in the design brief called for the installation of chemical filtration. In order to meet these criteria, the fresh air and recirculated air are passed through particulate and activated carbon filters. In October 1990, after the building had been sealed but before the air-conditioning plant in the new wing was commissioned, the NO_2 levels in various spaces were measured. The measurements were repeated in February 1991 after the plant had been operating for approximately two months and again in March 1992. The results are summarized in Figure 4. As might be expected, before the plant was commissioned the NO_2 levels in those rooms which were destined to be air-conditioned differed little from the levels in the rooms that were to remain without air-conditioning. The difference in NO_2 levels in these two types of room was apparent after the plant had been in operation for two months. A year later the difference was more marked, perhaps because in February 1991 the filters were still affected by the large volumes of dust in the newly finished building.

During 1992, a diffusion tube type passive sampler was used to test the levels of SO_2 . During the two week test period the exterior SO_2 level was found to average $24.8 \mu\text{g m}^{-3}$. A level of $11.8 \mu\text{g m}^{-3}$ was measured in spaces without air-conditioning, while those areas where the air was subjected to chemical filtration gave an SO_2 level of $2.1 \mu\text{g m}^{-3}$. The low levels of SO_2 in the air-conditioned rooms agree with the findings of the earlier studies at the Tate Gallery and National Gallery of Ireland, while the indoor/outdoor ratio for the non-conditioned areas is similar to the average value reported in a recent study in Florence (7, 10). The cumulative exterior level ($24.8 \mu\text{g m}^{-3}$) is lower than during any of the measurement periods in the previous study in London, which were selected to maximize the exterior SO_2 concentration (7). The lower level may also reflect a reduction in the atmospheric SO_2 concentration due to a decrease in the burning of sulphur-containing fuels or the very wet weather during which the readings were made.

Lighting design

The lighting design in the Sainsbury wing was influenced by the decision to use daylight to the greatest extent possible and to preserve its variety and changeability. In order to achieve satisfactory conditions for both viewing and con-

servation while allowing for natural variation in the level of daylight, the rigid maximum limit of 200 lux was dispensed with and an annual maximum exposure of 650k lux-h was set, in accordance with the specification for a Class 1 museum. The light in the galleries can thus be influenced by the movement of the sun across the sky or passing clouds. The natural light is supplemented when necessary by artificial lighting.

As mentioned in an earlier section, the specification for ultraviolet radiation was reduced from 75 to 10 $\mu\text{W lumen}^{-1}$.

Before the natural and artificial lighting systems were finalized, they were tested using a 1:5 model built on the roof of the National Gallery and a full-scale model at Shepperton studios in west London. In each case, a portable light-level logging equipment was used to produce a record of light levels and to allow the lighting scheme to be refined.

The lighting scheme

Details of the lighting installed in the Sainsbury can be found elsewhere (11). Only the aspects of the scheme concerned with the conservation of the collection are described here.

Daylight enters into a series of chambers located above the galleries. The outer roof is double-glazed, one of the layers being a laminated glass containing a polyvinylbutyral (PVB) interlayer which absorbs all ultraviolet radiation with a wavelength less than 380 nm and over 50% of radiation with a wavelength of 400 nm. The light entering the roof space is modulated by a bank of motorized louvres positioned directly beneath the outer glazing before it passes into the gallery through a series of diffusing clerestory windows. Early in the design phase, the use of photochromic glass was investigated but rejected on the grounds of an inadequate range of transmittance. The louvres serve two functions: to reduce the levels of daylight during periods of bright weather and to provide a complete blackout of the galleries when they are closed. The blackout is an important feature of the system, since it prevents light from entering the rooms during long summer evenings. The consequent reduction in exposure helps to compensate for short periods of high light levels caused by the less stringent control of daylight during the day.

Four of the galleries have windows onto the main staircase. The glazing in these windows also contains an ultraviolet-absorbing interlayer. Each window is fitted with a translucent blind to allow the level of light to be moderated when the gallery is open and an opaque roller shutter to exclude all light when the galleries are closed.

Picture lighting is provided by low voltage tungsten-halogen lamps fitted with lenses that distribute the light more evenly across the wall. The lenses are coated with a mixture of metal oxides which reduces the ultraviolet content of the light reaching the paintings to well below 10 $\mu\text{W lumen}^{-1}$ (2).

The artificial lights are also controlled by BMS. In each room, six light sensors constantly monitor the light level on the wall at the height of the paintings. If the average level of light on the wall over a period of time drops below a set level, currently 150 lux, the lights are switched on. When the average light level exceeds a second set value (250 lux), the lights are extinguished. The averaging procedure is intended to ensure that the lights do not switch on and off in rapid succession in response to small changes in the natural light.

The fragile chalk and charcoal drawing, *The Virgin and Child with Saint Anne and Saint John the Baptist* by Leonardo da Vinci, is displayed in a showcase at a light level of 45–50 lux. Uniform illumination across the surface of the cartoon is provided by light focused from a number of fibre-optic bundles mounted around the perimeter of the case. The tungsten-halogen light source is located well away from the cartoon to minimize its heating effect while the light-transmitting fibres absorb the ultraviolet radiation emitted by the lamp.

To allow the success of the control regime to be assessed, the readings from the light sensors are stored by the computer for weekly and annual analysis.

Testing the lighting

The test programme for the lighting was similar to that for the environmental control system. The sensors were first checked against calibrated instruments, and the readings from the BMS were compared with readings made in the galleries. The operation of the louvres and switching of the lights were tested next. Finally, the rooms were monitored over a period prior to the opening of the wing to ensure that the system operated correctly. Small changes to the switching sequences for the artificial lights were made as a result of these tests.

Conclusion

The design and testing of the environmental and lighting conditions in the Sainsbury wing were greatly simplified by the inclusion of very specific requirements in the design brief. The computer-controlled air-conditioning and lighting systems proved to be capable of providing the required conditions, although their long-term reliability cannot yet be assessed. The testing procedures set up for the Sainsbury wing, including the building of scale models, are now used routinely for refurbishment projects in the other rooms. The use of diffusion tubes to analyse chemical pollutants has been extended to allow routine assessment of the performance of the chemical filters on the air-conditioning plant and to give advance warning of the need for replacement.

More than a year after the wing first opened, the results from the computerized logging indicate that the conditions in the rooms are maintained within the specification in the original brief. Figures 5 and 6 show representative analyses

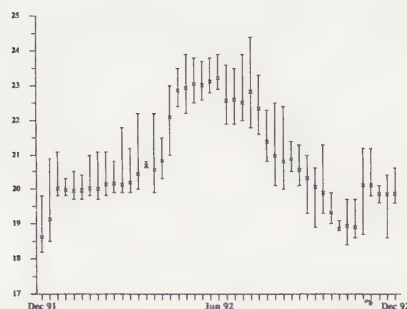


Figure 5. Maximum, minimum and average (X) weekly temperature (°C) for one room in the Sainsbury wing during 1992.

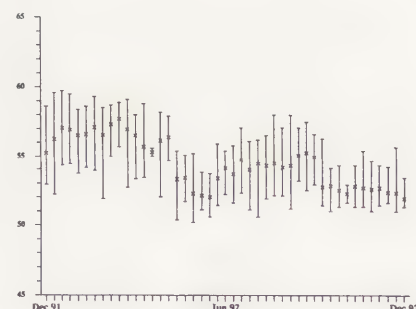


Figure 6. Maximum, minimum and average (X) weekly RH (%) for one room in the Sainsbury wing during 1992.

of the temperature and RH in one of the rooms. The temperature and RH are within specification, with acceptable variations between the minimum and maximum values in any particular week. There is considerable variation in the average RH values between weeks (up to 4%) and the transition between the winter and summer temperatures does not appear to be as smooth as might be expected. We have found the annual light exposure to be less than 650k lux-h. Although the weekly cumulative exposure during the summer months is generally slightly higher, this effect is mitigated by the uniformly low quality of English weather.

As a result of these studies, some small adjustments to the control parameters have been made to improve or simplify the operation of the air-conditioning plant and the switching of the lighting.

Acknowledgements

I am grateful to Alan Pepper of Ove Arup Partners and to Frank Brown, chief engineer at the National Gallery, for supplying information on the Sainsbury wing air-conditioning systems.

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Working Group 18

Conservation of Leathercraft and Related
Objects

Conservation des cuirs artisanaux et objets
similaires



Abstract

Until now the determination of the content of soluble sulphate was—together with other measurements such as pH, shrinkage temperature, and ammonia content—an indication of the degree of degradation of old leather objects in need of conservation. Such information might also indicate the resistance against deterioration of newly made commercial leather for conservation purposes. Analysis of sulphur content of new and old leather in different forms, has shown that a considerable amount of sulphur present in the leather appeared to be bound to the fibres. The consequences arising from this conclusion will be examined in the second part of this project, which will include methods of artificial ageing and a comparison of the durability of commercial bookbinding leathers.

Keywords

Leather, degradation, sulphate, analysis

The Sulphur Content of New Commercial Leather for Bookbindings

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Introduction

The cause of the strong deterioration, "red rot," of many leather objects has never been fully investigated and was connected to mainly metropolitan air pollution already in the last century in Europe. Then, as now, the problem was most pronounced in archives and libraries. In particular, leather bindings (but, in general, vegetable tanned leather from last century) clearly presents the greatest deterioration problem. The cause of the decay is ascribed mainly to air pollution, but there are strong indications that factors connected to the manufacture of leather also play an important role. This fact coincides with the introduction of new methods and materials for leather production by European tanneries in the last century (1, 3).

Recently, the Central Research Laboratory for Objects of Art and Science together with the Royal Library in The Hague, conducted an inquiry among conservators from libraries and archives to find out about their experiences with available new bookbinding leather. In some European countries, this type of special bookbinding leathers is commercially available.

One general remark that emerged from the answers was that the data available for the new leather were incomplete, for instance with regard to the applied tanning materials. A majority of the conservators also stated that there was a marked difference between leather from bookbindings manufactured according to traditional methods and recipes, and leather manufactured in the industrial era and later. The first type of leather bindings appeared to be much more resistant to atmospheric pollution.

As a result of this inquiry, we contacted several leather manufacturers and tanneries to enquire if they were able to produce a new calfskin leather according to the old recipes, without the use of any sulphur-containing chemicals and strong mineral acids, completely vegetable tanned (no combination tanning) with the right type of tanning material.

Finally, one small tannery succeeded in the production of a new calfskin leather according to the old recipes. In the first part of this project a sample of this leather is chemically tested for the presence of soluble sulphur compounds and the total amount of sulphur present together with six new commercially available bookbinding leathers.

We came across some specific problems in our negotiations with the tanneries. First, for dehairing skin, it is currently a normal practice to use small quantities of sodium sulphide to speed up the process. The use of lime only, as in the original recipes, makes the process temperature-dependent, and for successful dehairing (particularly during the wintertime), this could prolong the process up to six weeks. Besides, special dehairing machines are needed. Second, for deliming there is no need for the use of sulphuric acid or sodium hydrosulphite; these sulphur-containing chemicals could easily be replaced by lactic acid, for instance.

Third, in the process of bating, enzymes have been used for centuries; dog dung was used in the past. Today pancreatic enzymes are most commonly used, but most of them would also contain ammonium sulphate as a buffer salt to adjust the pH during that process. The ammonium sulphate, which is an unstable, inorganic sulphur-containing salt, should be replaced by another buffer, for instance an organic buffer, a citrate, or a lactate.

Finally, concerning the process of pickling, the word "pickling" refers to the

use of acids in this part of the procedure. For instance, it must be possible to use formic acid instead of sulphuric acid. In general, most of the tanneries stated that there was no harm in the use of sulphur-containing chemicals such as sulphuric acid, sodium sulphide, ammonium sulphate, or sodium sulphite, because during the process they are neutralized and washed from the skin. This may be true, but we have already established that in several types of new leather, sulphate was present in the residue after complete hydrolysis of the leather. This means that during the process sulphate, sulphide, or sulphite is possibly bound to the fibres and cannot be removed by washing. There are indications that these physically or chemically bound sulphur-containing ions will separate from the fibres during natural ageing and accelerate the degradation process.

Determination of soluble sulphate and soluble sulphide content

The analysis of the soluble sulphate and soluble sulphide content was performed with ion-selective electrodes in a watery suspension of sample material. The instrument used in combination with the specific electrodes was the Orion 960 autochemistry system, specially designed to enhance and expand electrode measurements. In the autochemistry system, eleven analytical techniques were programmed, achieving faster response, better precision, and reliability. The heart of the system was an expandable analyzer, a pH/ISE meter. Standardizing solutions and/or reagents were automatically added to the sample, and the concentration was determined from the changes in potential after each step. The results were automatically verified in two ways. A check for electrode drift and noise was performed at the beginning of each analysis. Each sample was spiked with standard as part of the analysis and recovery of the spike was calculated. Also, determination of very low concentrations of ions was possible, in favour of the amount of sample material.

By the determination of the sulphate and of the sulphide content in leather samples, the technique of "multiple known addition" was used. This is essentially a technique of adding small aliquots of the standard reagent to the sample, and calculating the original sample concentration from the observed changes in mV potential.

This technique helped minimize matrix effects and offers greater precision than direct calibration measurement, because calibration and determination of electrode slope and E_0 were performed directly in the sample matrix during analysis. The lead electrode used for the determination of the sulphate content, was a sensitive endpoint detector for titrations of sulfate ions with lead perchlorate. The method was simpler and less time-consuming than sulphate determinations by the gravimetric or turbidimetric methods, yet offered the same or greater precision in solutions as dilute as 10 ppm sulphate ion (2).

Preparation of the samples

A quantity of approximately 0.100 grams of material was collected in the form of loose fibres by scraping a vertical cross section of the sample removing the surface layers. This quantity of material was diluted with an amount of 50 ml of distilled water (4).

Determination of soluble sulphite content

The semi-quantitative determination of the content of soluble sulphite was determined by means of a colour test. The percentage of sulphite present in the sample was estimated by examining the discolouration of a reaction strip impregnated with sodium nitroprusside, potassium hexacyanoferrate, and zinc sulphate. The colour of the strip changes from pink to brick-red, depending of the concentration of the sulphite ions present. The pH value of the solution to be tested should be between pH 6 and 12.

Energy dispersive X-ray fluorescence

The preparation of the samples is identical to the determination of the sulphate and sulphide content. The determination of the total amount of sulphur in all

forms, free and bound to the fibres, regardless of the chemical formula in which it is present, is performed with X-ray fluorescence spectrometry.

Energy dispersive X-ray fluorescence provides a simultaneous qualitative analysis for all elements from sodium to uranium nondestructively. High energy X-rays, provided by a low power X-ray tube operating at a voltage from 5 to 50 kilovolts, are directed on a sample. The incident X-rays are absorbed by atoms in the sample and produce fluorescent X-rays. The X-rays coming from the sample are sorted by energy using a solid state detector, and appear as a histogram of X-ray intensity versus energy. The position of each peak in the X-ray spectrum provides qualitative information about the sample; the intensity of the peaks provides quantitative information.

Since the intensity of the peak is generally proportional to the concentration of the element, quantitative analysis can be performed by measuring a suite of well-characterized, similar type of standards and plotting a calibration curve. In many applications, such as the analysis of brass or bronze, a suitable set of standards can be purchased. Other applications, such as pigments in paints (and in this case, metals in leather) may require a suite of custom-made standards for calibration of the spectrometer. Recent advances in computer software used in energy dispersive X-ray analysis reduces or eliminates the need for expensive standard reference material that is difficult to obtain.

Low energy X-rays are strongly absorbed in air and by the beryllium window used by the detector. While bulk samples containing the elements from titanium to uranium can be characterized from a few parts per million (ppm) to 100% in air, the elements from sodium through calcium require a helium path accessory.

Elements below sodium are not normally detected using energy dispersive X-ray fluorescence. Similarly, thin films can be characterized in thickness ranging from a few micrograms per square centimeter to a few microns. (X-ray fluorescence spectrometers measure mass per unit area, usually expressed as milligrams per square centimeter; to convert to linear units such as microns a density must be assumed). The composition of thin films can be characterized from a few ppm to 100%, as with bulk samples. The maximum thickness which can be measured ranges from about 2–20 mg/cm², depending on the matrix and X-ray tube conditions used (5).

No sample preparation is required, as the analysis is nondestructive. The analyzed spot has a diameter of 2 mm² for all the samples.

Materials

Several leathers were tested (Leathers 1–7). Leather 1 was new leather, produced according to the following recipe:

Soaking:	water + 1% wetting agent
Paint to remove hair:	Na ₂ S + NaOH
Resulphide:	Na ₂ S + NaOH
Delime:	ammonium chloride
Bate:	pancreatic bate
Pickle:	NaCl, formic acid, and hydrochloric acid
Depickle:	sodium formate and sodium bicarbonate
Tanning:	sumac powder
Fat-liquoring:	synthetic fat-liquor

The tannery stated that there was no real alternative for the use of sodium sulphide in the dehairing proces.

Leather 1 was compared with the following commercially available new leathers for bookbinding:

Leather 2—Pessers
Leather 3—Glaser

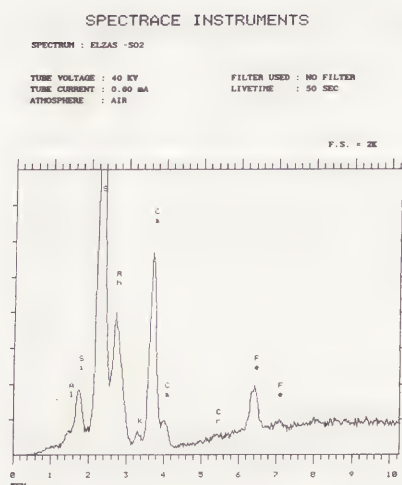


Figure 1. Graphical presentation of qualitative presence of metals by X-ray fluorescence spectrometry in leather sample, manufactured according to special recipe.

Leather 4—Hewitt 1
Leather 5—Hewitt 2
Leather 6—Elzas 1
Leather 7—Elzas 2

There was no additional data available on these types of imported new leathers.

Results and conclusions

First, the qualitative presence of metals was determined for all the materials in order to determine the elements necessary for the quantitative determination program (See figure 1).

For the determination of the total sulphur content, two reference samples were used. The content of metals present quantitatively was determined by means of atomic absorption spectrometry. The organic mass of material of the leather was calculated as 100%, minus the amount of metals present and expressed as C (See table 1).

Table 1. Total sulphur by X-ray fluorescence—reference materials.

ED-XRF Analysis	
Procedure:	Leather standardization 2 + 3
Filter used:	Pd thin
Tube voltage:	30 kV
Atmosphere:	Helium
Tube current:	0.02 mA
Count rate range:	medium
Lifetime:	100 seconds
Analysis method:	Fun. Params.
Preset count:	0 K
Standard H 13 layer 1 at 252.800 mg/cm ²	
S	1.700
Al	0.000
Si	0.000
K	0.080
Ti	0.000
Fe	0.007
Mn	0.008
Zn	0.003
Cr	0.000
Cu	0.006
Ca	0.012
C	98.184
Total	100.000
Standard H 14 layer 1 at 41.800 mg/cm ²	
S	0.070
Al	0.003
Si	0.002
K	0.002
Ti	0.000
Fe	0.022
Mn	0.002
Zn	0.003
Cr	0.000
Cu	0.008
Ca	0.006
C	99.882
Total	100.000

Table 2 represents the quantitative results of the determination of the soluble sulphate, soluble sulphide, and soluble sulphite content in leather sample No. 1 (manufactured according to a special recipe) and samples Nos. 2-7 (new bookbinding leathers) in % w/w.

Table 2. Soluble sulphate, sulphide, and sulphite content expressed in % w/w.

Sample	Sulphate	Sulphide	Sulphite	Total
1	0.09	0.04	n.d.	0.13
2	0.09	0.05	0.02	0.16
3	n.d.	0.06	n.d.	0.06
4	n.d.	0.08	n.d.	0.08
5	0.05	0.08	0.05	0.18
6	0.07	0.05	0.04	0.16
7	0.03	0.14	n.d.	0.17

Table 3 represents the quantitative results of the total sulphur content and trace elements present in sample No. 1 and the other six new bookbinding leathers, determined by X-ray fluorescence spectrometry and expressed in % w/w.

Table 3. Total sulphur and metals by X-ray fluorescence expressed in % w/w.

Sample	S	Al	Si	K	Ti	Fe	Mn
1	2.71	0.02	0.03	0.04	tr.	0.03	0.01
2	0.91	0.04	0.07	0.09	tr.	0.01	tr.
3	1.97	tr.	0.01	0.17	tr.	0.03	tr.
4	2.62	0.03	n.d.	n.d.	tr.	0.01	tr.
5	0.66	0.08	n.d.	tr.	tr.	0.02	tr.
6	2.99	tr.	0.03	0.12	tr.	0.03	0.01
7	1.59	n.d.	0.08	0.08	tr.	0.02	tr.

Sample	Zn	Cr	Cu	Ca	C	Layer (mg/cm ²)
1	n.d.	tr.	n.d.	0.05	97.09	9.85
2	tr.	0.29	0.01	0.01	98.55	56.97
3	0.01	0.02	n.d.	0.02	97.77	12.03
4	0.04	0.01	n.d.	0.01	97.29	9.06
5	tr.	tr.	0.03	n.d.	99.19	114.51
6	0.06	0.01	n.d.	0.05	96.69	11.54
7	0.01	0.24	n.d.	tr.	97.96	49.69

The detection limits for the elements are expressed in % w/w:

S	Al	Si	K	Ti	Fe	Mn	Zn	Cr	Cu	Ca
0.01	0.01	0.03	0.03	0.04	0.008	0.02	0.005	0.007	0.002	0.007

Table 4. The soluble sulphur and total sulphur contents are expressed in % w/w.

	Soluble sulphur content in % w/w	Total sulphur content in % w/w
1	0.13	2.72
2	0.16	0.91
3	0.06	1.97
4	0.08	2.62
5	0.18	0.66
6	0.16	2.99
7	0.17	1.59

Table 4 shows a direct comparison of the total soluble sulphur content of the seven samples and the total of free and bound sulphur in % w/w.

For all the samples, the measured amount of total sulphur is a factor 5 to 30 higher as the measured amount of soluble sulphur (See table 4). In some cases (sample Nos. 1, 4, and 6) the amount of total sulphur in the new leather is presumably higher than in degraded old leather. The measured amounts of soluble sulphate are small, and were considered residues of the chemicals used in the consecutive steps of leathermaking. The same applied to the measured amounts of sulphide and sulphite (See table 2).

From the recipe of sample No. 1, it is clear that in two consecutive steps, sodium sulphide has been used for dehairing, in spite of the fact that the leather was to be made entirely without any sulphur-containing chemicals. In this case, the measured amount of total sulphur compounds is 20 times as much as the measured amount of soluble sulphur. Although from the six commercial bookbinding leathers no data or recipes are available it may be stated that when sulphur-containing chemicals are used a considerable amount of sulphur appears to be chemically or physically bound to the fibres. The direct or indirect effect of this amount of bound sulphur on the process of degradation will become clear in the second part of the project, when artificial ageing in different stages will be applied to the samples and chemical and physical tests will be performed. Also, the effect of the occasionally rather high percentage of iron in connection with the acceleration of the oxidation of sulphur to sulphuric acid will be examined.

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Abstract

Textile objects incorporate a wide range of collagen and keratin materials. This paper discusses feathers and baleen, two keratin materials frequently encountered in textiles and treated by conservators of textiles and organic materials. The purpose of the paper is to broaden conservators' awareness of these materials, discuss potential problems, and offer possible solutions where appropriate.

Keywords

Keratin, feathers, baleen, whalebone

Feathers and Baleen, Two Keratin Materials Found in Textile Objects

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Introduction

To date, most published work on the conservation of feathers directly relates to ethnographic objects and natural history specimens (1–3). Baleen has been discussed only in relation to ethnographic objects and as highly degraded archaeological material (4).

The focus of this paper is feathers and baleen, two chemically-related keratin materials incorporated into textile objects. Feathers are directly woven into the textile structure, used in embroidery, or most commonly, applied as decoration on costume objects or accessories. Baleen is incorporated into the structure of costume, and occasionally used for accessories and in furniture.

Keratin

Keratin is the generic term applied to chemically-related resilient protein materials including hair, scale, hoof, horn, nail, claw, beak, and feathers. All keratins contain significant amounts of sulphur that crosslink and stabilize the material. The keratins are subdivided into two groups: soft keratins (epidermis or surface skin layer) and hard keratins (hair, horn, etc.) containing more than 3% sulphur.

The amino acid composition of keratin is complex and has been described by Vincent (5). All keratins contain a significant amount of the amino acid cystine, which serves as a covalent chemical linkage between adjacent protein chains of the material.

Horn and feather are composed of micro- and macrofibrils. About half the protein forms an extended structure in which adjacent protein chains associate with each other through hydrogen bonding to form a "pleated sheet" type structure. The remaining protein chains are more randomly bonded to form a more amorphous matrix.

Most hydrogen bonds are disrupted at temperatures between 40–60°C, which is why heat or steam can successfully be used to relax keratin, making it more pliable and allowing it or objects made from it to be shaped or moulded.

Keratin is remarkably chemically stable to changes in relative humidity (RH) and not easily damaged by chemical attack. It is, however, damaged by strong acids and alkalis and is particularly vulnerable to poor handling practices and insect attack.

Feathers

As decorative elements of textiles, feathers have been used whole, singly or in bundles. The cut pieces or individual fronds of feathers have also been incorporated into an object (See figs. 1, 2).

When whole or partial bird skins are used, they are most likely to have been prepared simple drying after skinning, or using standard taxidermy preparations and methods of the period. Mixtures incorporating arsenic and powdered alum or mixtures of arsenic, camphor and soap were in common use by taxidermists in the late 19th and early 20th centuries (6, 7).

The possibility of the presence of arsenic, albeit in minute quantities, should be borne in mind when handling whole birds, and appropriate care should be taken. The presence of arsenic in specimens may be determined using X-ray fluorescence analysis.

Because whole or partial bird skins were not preserved by tanning, if aqueous



Figure 1. Cape by August Champot Paris, ca 1895, (T84–1968). The cape is made of black and green cock feathers mounted in bunches and tufts onto cotton ground fabric and lined with silk satin.

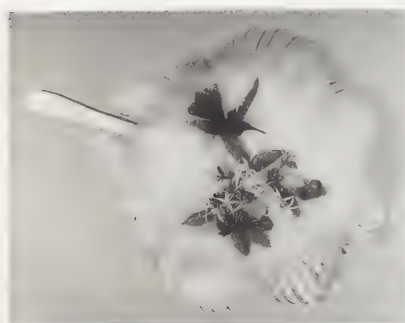


Figure 2. Feather Fan, Brazilian, 19th century, (T14–1950). Circular fan of white feathers with an ivory handle, decorated with sprays of flowers, leaves and berries made of white, red, and green feathers, and a stuffed hummingbird.

cleaning methods are considered for objects incorporating these, it is important to keep the aqueous solutions away from the skins and to use them with great care if cleaning the feathers still *in situ* on the skins.

Colours and methods of use of feathers

Although keratin is a chemically stable material, light will fade the colours of feathers, and exposure to continuous excessive heat will cause drying and embrittlement. A stable environment with a light level of 50 lux, temperatures of approximately 19°C, and relative humidity levels of approximately 55% is therefore recommended for feathers on permanent display.

When feathers are chosen for inclusion in a textile or costume object, the visual appearance is of primary importance. Some may be plumose and fluffy, some pennaceous and smooth, and some have upright barbs giving them a velvet-like pile as in an owl feather. All types of structure may be damaged by insensitive handling, especially when the feathers are in dry or degraded condition.

Feathers occur in all manner of colours. In nature, melanins and carotenoids are the natural pigments: melanins produce the dull yellow, brown, and black colours while carotenoids produce the bright yellows, orange, and red colours (8).

For whites, blues, and iridescent colours, the feather's physical structure plays an important part in combination with the pigments present. The surface layers of keratin have a structure of air-filled spaces that present an enormous number of reflecting and refracting surfaces. The whites, blues, and iridescent colours are produced depending on the configuration of these surfaces and the natural pigments present (9).

In the most favoured feathers used for costume and accessories, however, the colours produced in nature have never given sufficient variety to meet the needs of fashion; therefore, a number of different dyes—both natural and synthetic—have been used to artificially colour feathers. The exposed parts of dyed feathers often fade due to years of exposure in bright light. Fugitive dyes may run in water, water/alcohol mixtures, or hydrocarbon solvents.

Historic evidence shows that feathers have long been dyed for fashionable use. Many surviving portraits of Queen Elizabeth I painted in the 16th century show the queen holding fans that incorporate green and pink ostrich feathers (10). For fashion purposes, feathers have also been artificially curled or trimmed to provide shapes not found in nature. The fronds of plumose feathers have sometimes been lengthened by knotting on extra fronds to double the length and give the effect of pronounced buoyancy as the wearers moved about. In some cases, the feather shaft may have been split along its length to facilitate ease of manipulation when a large feather was used tightly curled or twisted. With time and progressive degradation, the split shaft can become an area of particular weakness.

Tightly curled feathers are often found on hats that may have been damaged by crushing. If steam is used to reblock and reshape the hat, this process must be carried out while avoiding the feather trimming; if the feather is allowed to come into contact steam, the air spaces in the feather structure will quickly expand, undoing the curl. The recurving of these mistreated feathers is not always possible.

Tufts of soft down, particularly from water fowls, were knotted onto a base fabric to create a downy cloth; the fronds of plumose feathers were woven into the structure of fabrics, most notably Chinese Kesi (fine tapestry-woven silk fabrics) of the 17th to 19th centuries. Also, in the 17th century, iridescent peacock feathers were frequently incorporated into English domestic embroideries.

History of feather use

The extreme popularity of feathers, as well as the fashion industry of Europe and America in the 19th century was directly responsible for the drastic deple-

tion, and in some cases, near extinction of a number of bird species. Evidence of this slaughter can be found in costume collections in museums throughout the world.

A movement to protect endangered species was active as long ago as the mid-to late 19th century. In 1869, The Sea Birds Preservation Act was passed in England to control the slaughter of seabirds for millinery purposes (11). Birds from all over the world were used in fashionable dress including herons, rheas, birds of paradise, owls, jays, kingfishers and magpies (12). In 1888, a sale is recorded during which 30,000 humming birds were sold in one afternoon (13).

It is not necessary for a conservator to have special ornithological knowledge, but a general appreciation of the birds whose feathers may be encountered is useful. The most common species used for fashion purposes (apart from ostriches, pheasants, peacocks and domestic fowls) are now mostly protected. Birds once commonplace when the objects were made are now rarities and, in some cases, may be almost extinct.

The ethical question of using replacements for badly damaged feathers does not frequently arise, therefore, as same-species replacement is mostly impossible and replacement using feathers from an alternative species would not be correct or acceptable.

Conservation treatments of feathers

Various methods of cleaning feathers have been described in previous works, using dry vacuuming, aqueous, and solvent treatments, and by using ultrasonic cleaning baths (14–20). For instance, magnesium carbonate powder has been used to dry-clean feathers.

The choice of conservation method will ultimately be determined by the object's condition, how the feathers are incorporated, and the facilities available in the conservation studio.

Conservators may occasionally have to treat feathers decorated with painted designs. The treatment may include cleaning of painted and unpainted areas. If the vane has been disrupted, physical damage to the paint layer and feather may have occurred. Dry vacuuming or surface cleaning using aqueous treatments could be appropriate or, if the paint will permit, an alcohol/water mixture. To consolidate the paint, isinglass or Paraloid B72 could be used.

Repair of feathers

The repair of broken feathers has long been practised by falconers on their birds of prey. This was done of necessity, as a broken flight feather can radically affect the accuracy of flight line when the bird swoops to take prey.

In the 16th century, broken feathers were repaired using iron pins, dipped in sea water, as dowels. The pin quickly rusted inside the feather shaft, forming a tight grip and preventing the pegged-on replacement feather from loosening or twisting. Today, falconers use stainless steel pins or dowels made from a piece of pared-down carbon fibre fishing rod and cyanoacrylate adhesives. Falconers also collect all moulted feathers from their birds to ensure a ready supply of repair material.

Conservators use similar materials or pieces of feather shaft taken from any modern feathers that might be available to them. They also use a more readily reversible adhesive such as Mowilith 50 (an acrylic resin) in acetone, or Paraloid B72. These adhesives are chosen because a feather on a museum object would not be subjected to stresses comparable to those of a bird in flight. Feathers may also be repaired by splinting, using feather shaft splints adhered behind the breaks.

When feathers are coloured it may be necessary to mask the repair in order to create an aesthetically pleasing and inconspicuous result. Japanese paper painted to match the feather using water colour may be wrapped around or patched over the join and adhered with Mowilith 50 in acetone.

Some of the most serious damage to feathers in museum collections is caused by insect infestation. Regular inspection is essential, and the monitoring of insect activity in the galleries and storage areas using insect traps is advisable. Deep freezing of objects is now an accepted method of dealing with insect infestation (21–23).

Baleen

Baleen is usually referred to as “whalebone.” However, bone is primarily made up of crystals of hydroxyapatite embedded in a collagen matrix, while baleen is a keratinous material. Baleen is formed from an agglomeration of hair covered with horn and looks like horn.

It is found in the mouths of right whales and rorquals (two species of cetaceans), where it is formed into elongated triangular plates that are used as food strainers. Each whale has 260–360 of these plates along each side of the upper jaw, spaced at approximate 5mm intervals. They are 25–30cm wide at their base and can grow to 3–5 metres in length. The plates are graded in size, with the longest oriented in the middle of the series, diminishing in size towards each end (24, 25). The parallel hair fibres in baleen are evenly distributed so that a plate of baleen may be split along its entire length to any degree of thinness. Baleen is light, flexible and strong and occurs in the colour range of grey-black through to light brown.

History of baleen

Baleen is a versatile material that has been used for many purposes over the centuries as it could be cut, sawn, shredded, or moulded into a wide range of articles. Records show that “whalebone” was known in medieval times when it was used in shoes for stiffening (26). It was also used in the 17th century to make artificial ostrich feathers, providing a cheap alternative to the genuine articles which were extremely costly at that time (27). It is primarily in costume and accessories of the 18th and 19th centuries, however, where baleen is regularly encountered by textile and organics conservators.

The three periods in the 17th, 18th, and 19th centuries when hooped petticoats were worn by fashionable women directly correspond to the 3 peak periods of the whale fishing industry. The Great Right whale also known as the Biscayan whale (*Balaena glacialis*), and was hunted to the verge of extinction in the 17th century. In the 18th century the Greenland whale, also known as the Bowhead whale (*Balaena mysticetus*), was particularly valuable as its baleen plates were of high quality and measured up to 4.5 metres in length. The Bowhead whale was hunted again in the 19th century in the Arctic Ocean and established the American whale fishing industry, which declined after flexible steels were perfected and superseded baleen hoops for petticoats (28, 29). Baleen, however, continued to be used for corsets until the early 20th century.

In furniture, baleen was used like cane work to weave carriage backs and sides, as well as chair and sofa bottoms. When shredded, it was used for stuffing chair and sofa bottoms and backs at a lower price that made it preferable to curled hair (30).

Conservation and cleaning of baleen

Baleen will not be harmed by standard aqueous cleaning treatments for textiles. However, it is a hard material and, if left in the boning channels of a bodice when it is washed, may cause scuffing or tears in the wet and vulnerable fabric of the garment. It is therefore customary to remove the baleen prior to aqueous cleaning of costume.

Hydrocarbon solvents will not damage the baleen but, as above, any manipulation of the fabric during solvent cleaning could cause the baleen to tear or scuff the garment.

Baleen should not be left in a costume which is commercially “dry cleaned” (solvent cleaned), in a closed system machine. Heat is used to quickly evaporate

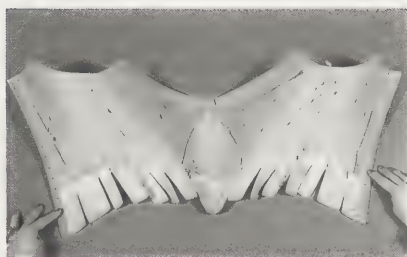


Figure 3. Corset, English ca 1770, (T56—1956). The corset fabric is cotton twill lined with linen. Fully boned with baleen, the corset is edged with white kid. The inner lining missing, so the details of the corset's construction may be seen clearly.

the solvent in these machines, and this could cause distortion of the baleen bones and possible damage to the object.

Corsets incorporating baleen are a separate case as it would cause damage to the corset to attempt to remove the baleen boning. There are no references in the literature to washing corsets containing baleen, but if the dyes in the fabric are colour fast and all the other incorporated materials are safe in water, there is no reason why it should not be possible to do so.

Repair of baleen

When a baleen rib or bone breaks across the grain, it is unlikely that it will snap cleanly; instead, it will split in a jagged way, tear, and possibly only partially fracture. This is in keeping with its laminated structure.

The repair to baleen must be strong; to hold the laminations together, the repair material must also have the flexibility to be harmonious with the nature of the material and be able to stand up to the stresses exerted upon it, e.g., when used for parasol ribs, the broken rib must be able to withstand the opening of the parasol after repair. The repair method should also not appreciably add to the thickness of the piece and it should be reversible.

An experiment was conducted to test five adhesives in common conservation use that meet these criteria and might prove satisfactory for baleen repair. The adhesives chosen were HMG (a cellulose nitrate based adhesive), "Super glue" (Loctite Prism 406 (a cyanoacrylate adhesive used with Loctite Prism 757 Primer), Mowilith 50 in acetone, (a poly(vinyl) acetate resin), Paraloid B72 in acetone (an acrylic polymer adhesive) and Araldite Rapid (an epoxy resin).

A baleen dress bone was used for the experiments. It was cut into pieces across the grain using scissors; the pieces were then bent by hand until they fractured. The broken areas were swabbed with acetone prior to repair in order to clean and degrease the surfaces. The cut pieces were taken and rejoined using each of the five adhesives. The adhesive chosen was applied to the butt end of each of the cut pieces to be joined and the ends were held together until they adhered. They were then placed on silicone release paper and left to dry thoroughly.

Once dry and after about 24 hours each piece was manhandled and lightly flexed. All the joins failed except the ones made using the cyanoacrylate adhesive and epoxy resin. These joins were subsequently manhandled and flexed until they failed, but the treatment they received was far in excess of that which an object should receive in a museum environment.

Next the jagged fractures were repaired using the five adhesives. Due to the fact that stretching and distortion of the baleen had occurred at the fracture sites, in some instances it was difficult to obtain a flat repair. When this was the case, the baleen was steamed prior to making the join in order to relax it and bring the two halves back into alignment. These repairs were carried out and left for 24 hours to dry thoroughly.

When the dried repairs were flexed and manhandled, the join repaired with HMG failed. The join repaired with Mowilith 50 in acetone also failed. The join repaired with Paraloid B72 held well, although when flexed aggressively, it too, weakened. The joint made with cyanoacrylate also held fast until it was severely manhandled, as did the join made with epoxy resin.

An experiment was also tried to reinforce a join by pegging with stainless steel pins. This proved totally unsatisfactory, as the baleen tended to delaminate and split along its grain as the pins were inserted.

It was concluded that the cyanoacrylate and epoxy resin adhesives provided the most satisfactory bonds for the repair of baleen. However, some reservations were held because it is known that cyanoacrylate adhesive becomes brittle and fails with age. It was therefore thought best to reinforce any repair made with this adhesive with a secondary support, possibly using a binding of gut membrane and Paraloid B72 or epoxy resin, or using splints of a stronger material such as pared down feather shaft adhered each side of the join. If necessary, these splints

could also be bound with adhered membrane. Additional practical experiments need to be conducted.

Conclusion

The treatment of feathers and baleen is not an everyday occurrence for textile conservators, but these materials can be found in textile and costume collections. Knowledge of their history of use, their properties and how to treat these materials is, therefore, vital information to anyone who may come encounter them in the course of their work.

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Abstract

The 18th century leather tapestries were mounted on all sides of a trunk and fixed with iron strips and clasps. Some of the tapestries were torn and deformed, and portions of the painted surface were flaking. Most of the ornaments were practically invisible because the surface was heavily stained and very dusty. Different methods of dry cleaning were tested. The use of an electric eraser with soft and hard mines was considered the most suitable. Using a Klucel G solution the flaking surface was stabilized. The tears and the craquelure were filled with Mowilith. The three advantages of this treatment were the effective and non-destructive dry cleaning method that did not require preliminary fixing of the uncleaned surface, the avoidance of the use of chemicals (and therefore, the lack of toxicity of the treatment as it affected the environment, the conservator, and the object), and the reversibility of the Mowilith adhesive.

Keywords

Leather tapestry, chest, paint layer, lac, dry cleaning, electric eraser, paint stabilization

The Conservation of the 18th-Century Leather Tapestries Covering a Traveling Chest

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Introduction

An ancient wooden travelling chest with a rounded lid joined to the chest by three iron hinges was the subject of this research. It was covered with pieces of leather tapestries with iron fittings and strips. The technological construction of the tapestries is a little different from the standard seen on other objects of this type, and is typical for leather tapestries from the 18th century. As most leather tapestries are in very bad condition, it was necessary to develop conservation methods for their preservation. While testing conservation methods, the efficiency of classic painting treatments were tested. Also, various rubbers were used for dry cleaning, an atypical cleaning method for this field. Portions of the tapestries were torn, deformed, and cracked, and the paint layers were flaking. The entire surface was very dirty, making most of the ornaments nearly unreadable.

Another issue to consider were the 25 meters of iron strips nailed to the chest. Their removal would have involved taking off hundreds of nails, thus unavoidably damaging both the strips and the tapestries. These considerations led to the development of a method of surface cleaning without chemical interference with the paint layer and leather itself. Other issues were the reduction of the use of toxic substances harmful to the conservator and the environment, and development of a way to remove deformations *in situ* without dismantling the tapestries from under the metal fittings.

Description of the chest

The object is a wooden chest with a convex lid covered with pieces of tapestries cut out of bigger panels. The tapestries are nailed with metal strips and reinforced with rectangles of sheet metal on the lid corners and around the side handles. The iron strips that are fixed to the chest are partly punched and tin plated. There are iron handles on both sides and a bronze lock at the front. The inside of the chest is lined with white linen on paper.

System of metal fittings

Strips of different widths are nailed with wrought nails and adorned with stipple (point) ornament of schematic grapevine twigs and a wavy line of flower fruit festoons. There are stylized bunches with stipple (point) ornament on the rectangular sheet metal fixtures. The nails are not spaced uniformly as a result of subsequent metal strip reinforcement carried out in the past with the use of additional nails. The strips embrace all the edges of the chest and divide the side surface into rectangular areas. The layout and proportions of the areas depended on the size of tapestry fragments. Two panels of preserved original width were tightened upon the centre of both the chest and its lid. On their sides, the side walls of the chest and its back, pieces cut out from other panels were tightened. These pieces are generally bigger than the fields between the metal strips. Markings of the panels are shown on the drawing (See fig. 1).

There are two squares (Aa, Ab) on the front side (A) spaced symmetrically in relation to the vertical axis, equal to the height of the chest. There are three small rectangles next to the edges of the chest, one over another. Five fields of tapestry are on the back of the chest: a square in the centre (Ba) and narrow, rectangular pieces on both sides (B1–B4). Each piece has the same height as the chest. Five fields of tapestry are on each side of the chest: a rectangle in the centre (Cd, Da) and two rectangles, one over the other on the outside (C1–C4, D1–D4). The lid of the chest is divided into 24 fields of nearly the same size by five vertical and three horizontal strips. Each of the corner fields is almost

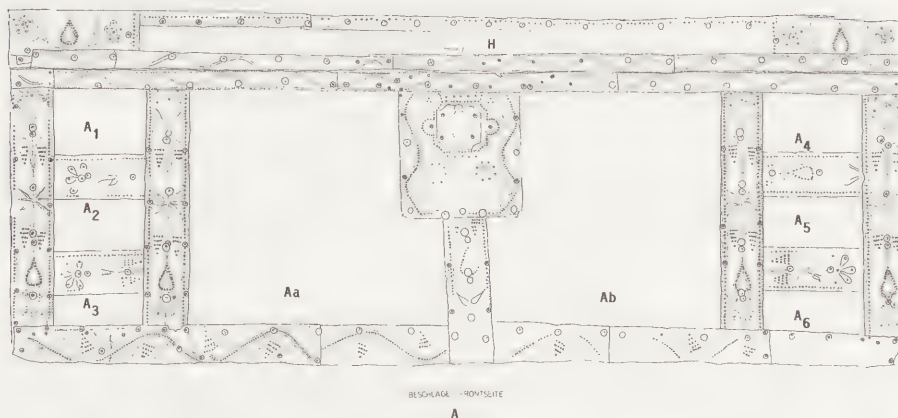


Figure 1. Cleaning and fixing of damaged lacs and paint layers on the leather tapestries.

completely covered by sheet metal of the fixings (E1-E24). The sides of the lid: (left f, right G) were divided into four parts with vertical strips. The corners have the shapes of irregular trapezia (F1-F4, G1-G4). The front of the lid forms a narrow, rectangular field.

Ornaments

There is a larger fragment of tapestry on the front side (A) in two central fields (Aa, Ab) with a theme of a precise double ribbon square as background. The sketch is drawn as if in two planes. One is created by a wider ribbon which draws diagonal squares, and the other by the meandering ribbon ornament intertwining and framing it. The background of each of the irregular square fields is hachured by a four-leaf flower alternately placed in the centre of the squares. This system of square sketches and fillings is the only possible way to determine the original pattern of the tapestry pieces. There are two compositions on each square: the flower passes into the fruit both of them being built on common meandering ribbons and "rocaille" themes.

Colours

The warm and saturated colours come from a very large palette of paint which was put on with clear brushstrokes, following the relief of the stamped ornament. The light and shade effects of the relief are bold and contrasting, often through the gradual fading of the original colour to white. Bright spots imitating light are very often applied.

Beside the realistic colours of fruit some fancy colours appear e.g., dark blue and red petals on the same flower. The flowers are mostly red and blue, the fruit gilt with the white glittering in the light.

Condition of the leather tapestries

The extent of damage to the tapestries on the individual sides of the chest varies. Those at the front are best preserved (front sides A and H) (See photo 1). The sides (left C and F and right D and G) are in poorer condition; the front tapestry at the back (B) and on the lid of the chest (E) show the worst damage (See photos 2, 3). Typical damage consists of distortion caused by shrinkage of leather and local tearing from under the nails, and severe splitting of leather as result of being fixed with nails and metal strips. In addition, shrinkage of the surface has resulted in tensions between layers of tapestry and paint; this has caused delamination and loss of layers.

The good condition of the tapestries on the front might be due to better conservation. The leather is tight and elastic. The surface of the front squares is more legible than any other area. The surface dirt includes well-adhered dust and sprinkles of wall paint. According to a report by the museum's director, these squares were cleaned by a paintings conservator about 15 years ago. The side squares are more grimy and similarly splashed with wall paint. The leather is slightly tensioned and shows deformations only on the middle of A and H



Photo 1. The front side of the chest before conservation.



Photo 2. The back side of the chest before conservation.

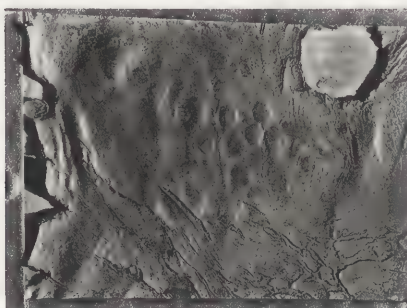


Photo 3. The damage of leather tapestry on the lid.

fields. The surface is scratched and scraped. Great losses of paint layers have occurred over an unidentified fruit above the horn of plenty (Aa), on the orange fruit, and on the background chequered pattern. An underlying light brown leather is visible beneath these losses. Silver glitters from under the losses close to the gilt ornaments.

The tapestries on the right (D, D) and left wall (C, F) are badly damaged. Their surface is so covered in dirt that the ornaments are illegible on some areas. The dirt consists of dust deposited on the surface and sprinkles of wall paint. The leather of these tapestries is harder, more deformed, cracked, and torn, whereas the bottom edge is frail because the metal border is missing. The dirt covers vast losses in the paint layer.

The tapestries on the back wall (B) are badly damaged. The leather is extremely fragile, often scratched, and loosened by tensions due to temperature and humidity changes (the back of the chest must have been placed close to the fireplace after journeys). Originally, each piece of tapestry covered the back of both the lid and the chest. Due to frequent opening, the leather was torn along the axis (horizontally) of the hinges. The central square is also torn in the middle from the top to the bottom. The leather is curled and the paint layer is peeling off, showing the silver and the white ground layer.

The tapestry on the chest lid is very concessioned with nails and metal bands. The leather became seriously cracked during shrinking. The network of cracks on some squares is similar to rifts on the ground burnt by the sun. The side pieces are held in place close to the lid edges only by nails. While shrinking, they became deformed and cracked. Only fragments of the paint layer remain on three pieces of the chest lid (over 50% loss). The presence of silver only in the ornament fields must be ascertained. These fields are not covered in paint, but only in gilded varnish; this is typical for French leather tapestries from the 18th century.

Conservation problems and the way to solve them

For this treatment, the conservation methods and goals included the following: 1) maintaining the original fixtures in their original positions without removal of the tapestries from the chest, 2) development of a method to dry clean surface dirt with the help of various rubbers without negatively affecting the structure of leather and paint layers, and 3) the reinforcement of cracks and delaminating paint.

It is not advisable to remove the original fixtures (about 25 m of metal strips and hundreds of nails) without a genuine necessity. The drawing documents not only the ornament strips but the position of nails and their types as well. The ornaments of individual squares have also been sketched. The sketches were subsequently united and the patterns were partially reconstructed. During this process it has been possible to ascertain that the tapestries were designed as panneaux with fruit and flower theme with an exceptional chequered pattern background.

As the tapestries at the back of the chest are badly damaged, it was determined that it was necessary to remove them. Only the oldest nails with rounded heads and conical pins were easily removed, whereas those with pins resembling wire have been stuck hard and fast into the wood and were difficult to remove; taking them out caused damage to the paint layer. Original nail positions were shown by hammering the nails into a drawing of fittings glued upon a board of polyurethane.

Dry cleaning

Then the surface of the leather tapestries had to be cleaned. Painting layers had started to peel off the silver layer and the only way to avoid further losses was by dusting with a soft brush, a traditional method in the conservation of paintings and polychrome sculpture. Another traditional method in this domain of conservation is wet cleaning with cotton buds and various solvents. Both methods, however, were ineffective. The first method does not clean the surface well

enough and the other method causes losses of tiny flakes of paint. An application of 2% Klucel G in water failed to make the paint layer more resistant to cleaning. The surface of the tapestries therefore remained dirty and the colours have not recovered their original intensity. A search for new methods began and techniques from field of paper conservation were applied, specifically, the manual and mechanical use of a variety of rubbers.

In the Paper and Leather Laboratory of the Museum Comission in Westphalia, rubber in both powder and solid forms is applied. Solid rubbers are the traditional materials, known from school days. Pencil-shaped rubbers wrapped in wooden or paper handles and refills for eraser machines and clic eraser were tested. Powder rubber was used loose, out of the container or in small sacks applied with cotton wool and granulated to be applied with micro sand blaster. An intermediate form between solid and powder rubbers is "wish ab" rubber, a cuboid-shaped material that is pulverized while rubbing.

The rubbers not only differ in form but in their material composition as well. They vary in hardness, which decides upon the efficiency of the rubber in relation to the surface being cleaned. Rubbers in powder form have an important disadvantage: they penetrate into the leather cracks making it impossible to remove them. They should be used exclusively on closed surfaces. A sand blaster was used to clean the surface of archaeological leathers excavated in Bocholt, in Westphalia.

The following erasers were tested on well preserved surfaces of the leather tapestry:

Name	Material	Form	Company
Supra 340	latex	block	Läufer
TK Vinyl 7081	vinyl	block	Faber-Castell
Clic Eraser Refill	vinyl	min	Pentel
Ecobra 3295	vinyl	min	Ecobra
Peel-off Magic Rub	vinyl	min	Faber-Castell

First the surface was cleaned manually with the erasers. To achieve a thorough cleaning, strong pressure had to be applied. As a result, the scales of the paint coating flaked off easily and the dirt remained. For that reason an electric eraser was used. Preliminary tests showed that mechanical erasing produces more heat. For a study of heat development, hard mines with filling materials that rub off the surface were sorted out, and the recommended eraser "Magic Rub" of the Faber-Castell Company was used. The softest mine on the market, Clic eraser

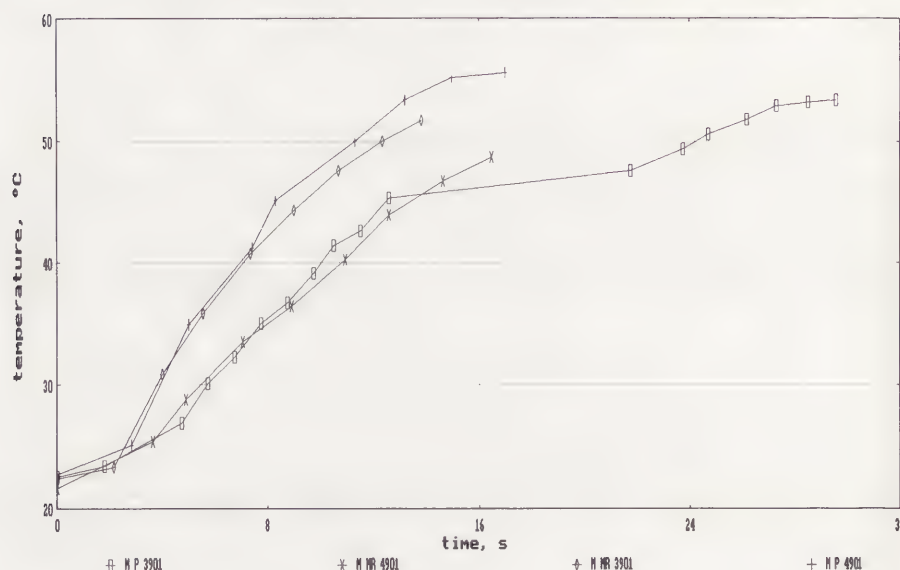


Figure 2. Heat development of erasers.

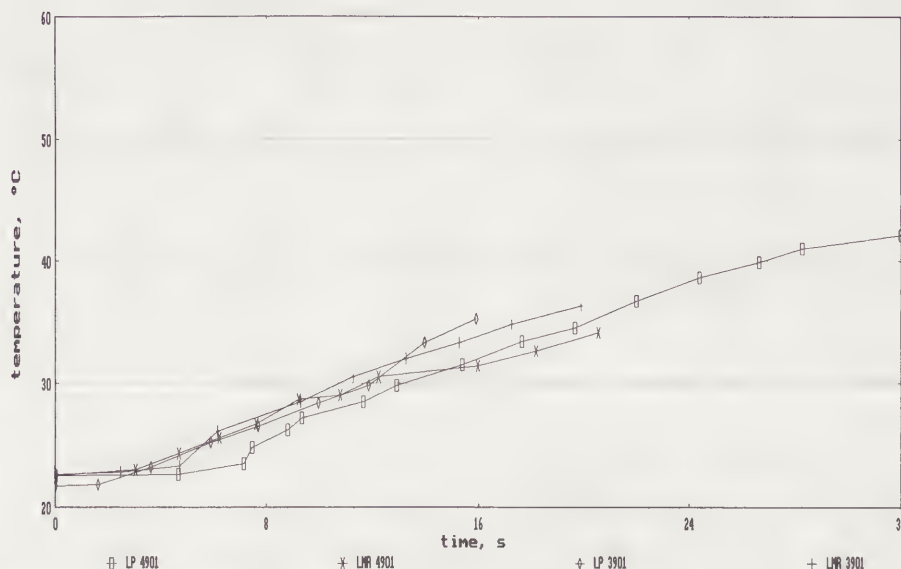


Figure 3. Heat development of leather.

Refill of the Japanese company Pentel, was employed. Two types of electric erasers produced by Ecobra were tested: "Ecobra 4901" (battery driven with 2500 revolutions per second) and "Ecobra 3901" (with a built-in 12 volt power pack and 1500 revolutions per second). The heat development was measured with a digital brass sensor thermometer "Ama digit 31th" (Ama Electronic). The time was taken with a stop-watch, and the data were registered photographically.

For the first test the eraser was used on the brass sensor (See fig. 2). After a short initial period the curves showed a quick rise in temperature. After four seconds, temperatures of 30°C were reached by Ecobra 3901 with Pentel and Ecobra 4901 with Magic Rub. A similar slower rise in temperature was noted with Ecobra 3901/Magic Rub and Ecobra 4901/Pentel.

The heat development in the leather shows a similar curve reaching 30°C after 12–14 seconds. (See fig. 3). The conductivity of the leather was fairly poor. It showed that the ideal eraser combinations are Ecobra 3901 with Magic Rub and Ecobra 4901 with Pentel. The most precise work can be done with Ecobra 4901 and Pentel. Photograph 4 depicts square no. A4 on the front side after partial dry cleaning. Photograph 5 shows the square on the side wall, also partially dry cleaned.



Photo 4. The square No. A4 on the front side; partly dry cleaned.



Photo 5. The square on the side wall; partly dry cleaned.

Stabilization of paint flakes

The method applied was tested in experiments by the Institute for the Conservation of Paper and Leather of the University of Torun. The entire surface of the leather tapestry between the iron strips and clasps was covered with Japanese paper, through which a fixing agent was applied with a brush.

For the stabilization of the flakes of paint, several consolidants were used that are common in the conservation of paintings, particularly parchment glue and sturgeon glue. These glues possess a natural affinity to the collagen fibres of leather tapestries. For the conservation of paintings, synthetic resins such as methylcellulose or Klucel (hydroxypropylcellulose) are used as well. The concentrations in water range from 0.5 to 3%. BEVA, a different fixing agent, is based on wax. Like conventional wax, it causes a strong darkening of the leather even after the very first tests. For the trunk Klucel G was chosen, because retouching with silver powder mixed with Klucel G as a bonding agent was planned for later in the treatment. The parts of the tapestry that had been lifted off the trunk were placed on a glass plate and covered with broad-rimmed Japanese paper through which glue was applied. Both the paper and leather expanded. During the drying process the leather shrank to its original size, but the paper stuck to the glass plate with its edges and tightened over the leather, thereby smoothing it down.

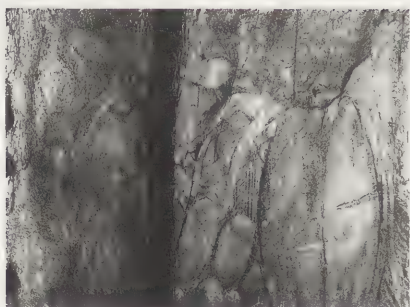


Photo 6. The squares from the back side; partial filling of cracks.

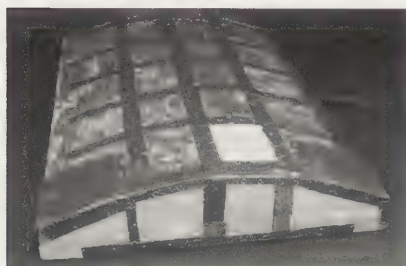


Photo 7. The fixing of the flakes of paint layer and smoothing down of leather in situ.

Filling the cracks

The method of filling the cracks in the leather and the paint layer is based on the experiences of the University of Torun as well. The poly(vinyl) acetate glue which is applied to the cracks and the craquelure in a thick layer was partly absorbed. The rest must be rubbed off with a finger during the drying process.

In this case, two kinds of Mowilith glue were tested. After the drying, Mowilith 105 forms an elastic thin coating, whereas Mowilith 1 forms a hard coating. During the tests, Mowilith 1 proved to be too hard and too brittle; it was also more difficult to rub off. As an illustration of filling, Photograph 6 shows the squares from the back, with partial filling of the cracks. Photograph 7 shows the stabilization of the paint layer flakes and smoothing down of the leather *in situ*.

Conclusions

Several conclusions can be drawn as a result of this work. On part of the trunk, it was impossible to keep the metal fixing and nails in position during conservation. Using the fast spinning Ecobra 4901 with the Pentel-mine, excellent dry cleaning results were obtained on both paint and silver layers on the tapestries. Preliminary fixing of the flaking paint layers did not seal the surface dirt at the same time. Finally, filling tears in the leather and paint layer with Mowilith 105 seals the surface and reduces the amount of retouching needed.

Acknowledgements

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Abstract

In the past, the leather used as wall decoration or as a painting support enjoyed periods of success and sometimes great splendor. At the Italian Central Restoration Institute (ICR) in Rome, the "Leather" Section has embarked on a project to develop a registration system for technical data. Such data will contribute to better knowledge of the few objects that are still extant, forestall the virtually total dispersion of unknown or unrecorded works, and suggest directions for future research. A brief description and a few examples of the registration form are given. Complementing the forms, a technical lexicon and a collection of graphic and photographic documents are supplied.

Keywords

Painted and gilded leather, leather wall hangings, tooled decoration, leather punches, technical lexicon, database record, image archive

A System for Data Collection for Skin and Leather Artifacts: I. Wall Hangings and Paintings

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Introduction

Leather wall hangings and paintings on leather are rarely studied today, nor have they received the attention they deserve, considering that leather, as a support for gilding and painting, enjoyed moments of great success up to the late 18th century. Even when its popularity began to decline, high-level works such as Guardi's series of altar frontals were still being produced.

From the mid-18th century on, leather wall hangings were supplanted by wallpaper, and they seemed to elicit only sporadic interest in the 19th century, when there was a sort of ephemeral revival, not exempt from a certain snobbery, among "cultivated" circles. There was an attempt to imitate entire leather-hung walls with paper, reproducing leather's salient characteristics, as in the surprising decoration of Palazzo Brancaccio in Rome.

From the few remains that have survived to the present day, it is more difficult than for other artistic products to provide a technico-historical framework that also takes account of temporal and geographical coordinates. What is needed, especially for Italy, is a "history" of this type of product, for which even the most generic survey is lacking on a national scale. Two centuries of indifference, combined with the intrinsic perishability of the material, have led not only to the loss of even the most basic information on the techniques of execution (even for important types such as flock leather), but the virtually total loss of the works themselves.

Therefore, in 1990, the ICR Section for conservation of artifacts in skin and leather decided it would be useful to develop a pilot registration project, the aim being not only to collect identifying data on the works that still exist, together with accompanying documentation (archival or printed documents, photographs, etc.), but also information on their techniques of execution and state of conservation.

Beginning in 1991, the study has concentrated on the regions of Umbria and Latium. A pilot database registration form was developed and will now be tested during field surveys. We hope there will be far more existing examples than the few that we have managed to discover so far. The form, itself, will be combined with a technical lexicon (development of a technico-historical lexicon is also planned) derived from printed or manuscript sources relating to the artifact being registered.

The registration form is described briefly in this paper. While the registration form's structure is still open to improvement, it is at least indicative of the concerns that are of interest to the Leather Section.

Finally, it seemed useful to communicate this activity to other members of the ICOM Working Group, to have their feedback, and perhaps to stimulate cooperation among laboratories so that the data collection will spread to the international level and at least the technical lexicon might become multilingual.

Structure of the registration form

The registration form, developed in DB3 and installed on an IBM personal computer, has a structure that meets particular exigencies of archiving. In developing a system for computer registration of leather artifacts, emphasis was given to a logical organization of the material collected, in order to facilitate

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data input and recovery. Two levels of information are involved: (1) a "basic level" for registration of information essential to defining the research areas identified (data elaborated in synthetic form and, therefore, easily recovered for research purposes); and (2) a "level of greater elaboration and detail" that completes, explains, and documents the basic information.

The research area chosen is that of leather furnishings, but we have not excluded the possibility, given a wider registration activity, of collecting information on other classes of leather artifacts, as well as works executed in other materials but belonging to the class of interior decoration and having typological and iconographic similarities to leather works.

For this reason, the form was organized into two communicating records. *Reference records* contain identifying data about the work (these records are applicable to every class and typology of artifact). *Analysis records* contain specific technical information (these records are structured for leather furnishings, in particular).

For registering the "basic" information in these records, the program has alpha-numerical fields of fixed length (from 2 to 256 characters, depending on the space necessary). Where there are fields that involve constant, codifiable entries (for example, component materials and execution techniques, typology of the subject and decorative motifs, structure of the artifact, etc.), the fields have authority files where the appropriate entry can be chosen.

In contrast, all the other information collected on the artifact in the course of research is entered in alpha-numeric cells of unlimited length (memo fields). These fields, in the layout of the form, are almost exclusively reserved for notes.

The data entries can be seen either as individual records, with the fields on several successive screens, or as lists which offer an overview of the information. In the lists, the data can be selected by fields of interest and/or sorted alphabetically to form indexes. The program can print either lists or forms. The form structure can also be modified in the print phase by selecting particular fields or only those containing data.

To recover the information registered, the records can be searched by either phrases or words in the individual fields, with no limit on the number of requests that can be made. To give the records a certain uniformity and permit objective recovery of the data, an inputting protocol has been drafted and will be tested and improved in the course of the analysis of the material as it accumulates. The standards are accompanied by a technical lexicon, now being defined, which will help to avoid the use of overly generic, inconsistent, or careless language in defining or describing either the artifact or the procedures used in making it.

The data registration will also involve some ad hoc, black-and-white documentation (which will subsequently be archived), obtained with a low-definition scanner in an image program, which can be linked to the record through the "documentation notes" field. This would include both photographs and graphics. Photographic documentation would include black-and-white and color, front and back of the object, full view and details relating to technique of execution, and state of conservation (tooling, inscriptions, seals, particular aspects of deterioration, etc.). Graphic documentation would include 1:1 restitution of the punches (possibly extended to basic decorative motifs) and a rough floor plan of the location in the case of wall hangings.

Transcription of bibliographic and archival references, as well as printed texts and manuscripts will be archived in a program connected to the record through the *Documentation notes* field.

The reference area of the form includes six search areas to identify the artifact—location, typology, attribution, iconography, documentation, and compilation—divided into 40 headings, eight of which are for notes. For brevity's sake, the description is given in Figure 1.

The analytical area of the form is a section that complements the reference area, in order to give more detail on some aspects inherent to the structure of the

artifact (materials and techniques of execution, in particular) and its state of conservation.

Designed especially for leather furnishings, this section is divided into 12 headings, three of which are for notes. The headings are as follows: characterization of the artifact, support, worked layer, decorative layers, support structure, attachment, techniques of execution, notes on the technique of execution, punches, notes on punches, state of conservation, and notes on the state of conservation.

The analytical section is not intended to cover the description of the work completely, as that might require a form designed specifically for the survey of techniques of execution and state of conservation, but simply to indicate a series of technical data that contribute to a better knowledge of the artifact and suggest areas where further research could be useful.

Structural composition of the artifact

The following headings allow for collection of complete information on the structural composition of the artifact (understood virtually as a group of layers): characterization of the artifact, support, worked layer, decorative layers, and support structure. The *Characterization of the artifact* heading will include identification of the layers present in the artifact under examination, described individually under the successive headings. The *Support* and *Worked Layer* headings both refer to the leather found in the structure of the artifact, sometimes as a support for decorative layers (for example, in gilded and painted leather wall hangings) and sometimes as a visible layer treated through surface working (for example, furnishings coverings in pressed leather). The headings allow for a description of the parts and/or elements that make up the two layers, with particular reference to the following: number and name of the parts (e.g., panels, friezes, strips, etc., for wall hangings), number and shape of the elements (skins), and assembly techniques.

The *Decorative layers* heading is reserved for registration of layers superimposed on the leather for decorative purposes, such as metal leaf, paint layers, gold paint, etc., listed by stratigraphic order from top to bottom and correlated to the component parts in leather (such as panels, strips, friezes, chair backs). The *Support structure* heading includes indications on the typology and component parts of any support structures.

As part of the characterization of the artifact, under headings regarding the layers, there is a heading for *Attachment* in order to indicate both the presence of structures to contain the work (e.g., frames) and systems of anchoring the support to the underlying structure (e.g., perimeter nailing).

The headings that follow in the analytical section of the form are supplied with authority files from which the subheadings of interest can be selected (from one to all depending on registration requirements), and flanked by memo fields for fuller written description of the *Notes* section.

Techniques of execution

The heading *Techniques of execution* supplies indications on production procedures and surface working of the leather parts of the artifact, already listed briefly under the headings for worked layer and decorative layers. The *Notes* section provides space for more detailed information, including data obtained both from direct observation of the artifact and from results of scientific analyses performed to characterize the component materials.

Punches

The need to insert a field for this item springs from the importance of this tool in the history of leather decoration, particularly for some types of artifacts such as wall hangings, bindings, boxes, etc. The heading allows for a first classification of punches by decorative motifs, subdivided into different classes. In the *Notes* field, one can register the number and description of punches found on the artifact. The description of the tooling, proposed by the compiler of the form

in the absence of standardized terminology, is accompanied by a reference number that refers to the graphic illustration of the punches and the related glossary.

State of conservation

The heading *State of conservation* furnishes general indications on the state of the artifact as a whole through a simple listing of the principal forms of deterioration found. These are pinpointed and quantified in the *Notes* field. In fact, for every type of damage, the layer of the artifact in question is indicated (support/worked layer, decorative layers, support structure) and the extent of the damage is expressed as a percentage.

Examples

A series of examples of the registration program is given in Figure 1. The use of italic indicates that the term has been included in the technical glossary.

Conclusion

In this paper, we have proposed a new system for collecting data about skin and leather artifacts. It is hoped this new system will improve present record-keeping procedures and facilitate exchange of information among conservators.


Table with fields selected from the reference section

Form n°	Province	City	Building and room	Component materials	Class	Typology and name	Measures	Century	Quarter of century
28	RM	Ariccia	palazzo Chigi, piano nobile, winter dining room	leather	furnishings	wall hanging in silvered leather, gilded, painted and tooled; "parato della Sala d'inverno"	c.80 m2	17c	III

Table with fields selected from the analytical section (form 28 contd.)

Characterization of artifact	Support	Decorative layer	Support structure	Attachment	Techniques of execution	Punches
- support - decorative layer - support structure - attachment	"panels": made of squared skins, cm 54x42, joined by sewing; friezes: made of squared skins, cm 41x42, joined by sewing; "panels" and friezes are sewn to each other	"panels" and friezes: metal leaf, gold varnish, paint film; impressions of punches; dominant color: red	wall	perimetrical nailing; nailing of the contact surface only in case of loss of the original assembly systems or of the mechanical damages	- tanned skin - silvered with silver or tin leaf - gilded with gold varnish - painted in oil - impressed with punches	- geometrical motifs
					Notes tanned skin: with tannins, oak painted in oil: with red lakes	Notes punches, n.5: - parallel lines (6a) - rooster's eyes (14d) - rooster's eye with double crown of points (8a) - waves (7) - mat (18a)

Glossary of punches (form 28 contd.)

Number	Graphic documentation Rubbings	Proposed name	Historical name	Measurement [in mm]	Principal use	Artifacts involved: typology and period
8a		occhio di gallo (rooster's eye) with double crown of points	unknown	10 (diameter)	surface tooling to accompany decorative motifs	form 28: wall hanging, 17c form 35: wall hanging, 17c form 26: wall hanging, 17c form 36: wall hanging, 17c

Photographic documentation (form 28)



a



b



c



d



e

ARICCIA, palazzo Chigi, winter dining-room: gilded and painted leather wall hanging, 17c.

Both for panels and friezes, the decorative module coincides with the size of a skin.

a) panoramic view b) panels: a skin c) panels: wood block d) friezes: a skin e) friezes: wood block

Figure 1. A series of examples of the registration program.

Résumé

La détermination des groupements N-terminaux peut être un outil pour caractériser la dégradation hydrolytique du collagène dans le cuir. La réaction à l'isothiocyanate de phényle (PITC) sur les extrémités N-terminales des chaînes polypeptidiques conduit à la formation de dérivés phénylthiohydantoïnes (PTH) différant suivant l'acide aminé concerné. Leur séparation par chromatographie liquide à haute performance, à polarité de phase inversée est réalisée avec un gradient de concentration de phase mobile en 15 min sur une colonne en C_{18} . Leur identification au moyen d'étalons permet d'évaluer les différents acides aminés N-terminaux de la protéine à un instant donné et aussi de déterminer par comparaison la progression des coupures des chaînes polypeptidiques. Une attention particulière est portée à la préparation du cuir en vue de son analyse. Les essais sont entrepris sur des cuirs vieilliss artificiellement et sur des cuirs anciens. Une méthodologie est proposée.

Mots-clés

Analyse, chromatographie liquide, HPLC, collagène, cuir, dégradation, isothiocyanate de phényle (PITC), phénylthiohydantoïne d'acide aminé (PTH), groupement (résidu) N-terminal

Etude du vieillissement des cuirs de tannage végétal: dosage par chromatographie liquide des groupements N-terminaux

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Introduction

Comme tout matériau organique, le cuir de tannage végétal est susceptible de se dégrader au cours de son vieillissement. Ceci est particulièrement préoccupant pour des objets dont on veut assurer la pérennité comme les reliures en cuir ou les cuirs archéologiques. La détérioration du cuir est le résultat des multiples coupures des chaînes polypeptidiques provoquant une désorganisation de la structure moléculaire. Elle se traduit par une perte de la résistance mécanique, par des changements des caractéristiques chimiques et de la température de rétraction. L'hydrolyse partielle des chaînes polypeptidiques survenue dans le cuir vieilli a pour conséquence l'apparition de nouvelles extrémités terminales. La détermination des résidus N-terminaux permet donc de quantifier les coupures de chaînes et de situer les lieux où elles se produisent. La reconnaissance de ces résidus ne peut se faire qu'après les avoir transformés en des dérivés facilement détectables.

Les principales méthodes reposent toutes sur un même principe mettant en jeu une réaction spécifique avec la fonction amine ($-NH_2$) terminale, suivie d'une hydrolyse acide qui conduit à la libération du résidu dérivé de l'acide aminé N-terminal de chaque chaîne.

Le chlorure de dansyle [1,2] et le DABITC [3] utilisés fréquemment pour marquer les protéines n'ont pourtant pas connu d'application sur le cuir. Par contre, le fluoro-dinitro-2,4 benzène (FDNB) ou réactif de Sanger [4] a été largement employé dans l'étude du collagène par Bowes et Raistrick [5] qui précisent toutefois que cette méthode n'est pas applicable aux cuirs végétaux à cause des interférences dues aux tanins. La méthode de dérivation à l'isothiocyanate de phényle (PITC) apparaît comme séduisante car elle permet d'obtenir des dérivés phénylthiohydantoïnes (PTH) également identifiables par des techniques d'analyse performantes comme la spectrométrie de masse. L'expérimentation portera sur l'application de ce réactif sur un cuir ancien et sur des cuirs vieilliss artificiellement. La séparation et l'identification des différents résidus N-terminaux présents se fera par chromatographie liquide.

Principe de la méthode

Une chaîne polypeptidique se présente comme un enchaînement d'acides aminés liés entre eux par des liaisons peptidiques. L'un des bouts présente une fonction α -aminée libre: il est appelé "extrémité N-terminale" et l'acide aminé portant cette fonction amine ($-NH_2$) libre "résidu N-terminal". De même, on a l'extrémité C-terminale représentée par le "résidu C-terminal" qui porte une fonction carboxylique ($-COOH$) libre (voir Fig. 1a). Une hydrolyse acide provoque une scission au niveau de la liaison peptidique, libérant à chaque fois une fonction $-NH_2$ et une fonction $-COOH$ et conduit à une fragmentation du peptide en unités plus courtes (voir Fig. 1b).

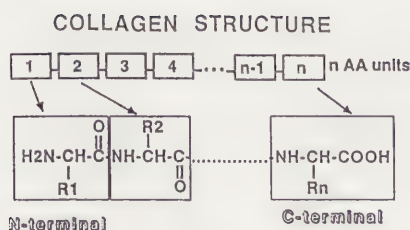


Fig. 1a: Structure du collagène

Le PITC se combine intimement et spécifiquement à toute fonction α -amine libre des extrémités des chaînes polypeptidiques, marquant ainsi l'acide aminé N-terminal que l'on détache alors du reste de la chaîne sous forme de dérivé stable et détectable: le phénylthiohydantoïne qui diffère suivant l'acide aminé. C'est le produit obtenu classiquement au cours de la dégradation d'Edman [5]. Cette réaction met en oeuvre plusieurs étapes (voir Fig. 2a):

1—le couplage mené dans des conditions alcalines au cours duquel le PITC réagit avec le groupe N-terminal pour former un dérivé N-phénylthiocarbamyl (PTC) de peptide. Cette étape est suivie d'un lavage pour retirer l'excès de réactif.

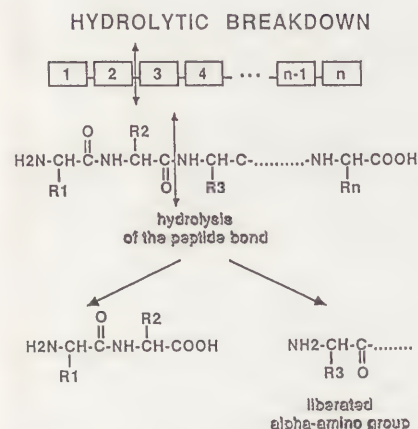


Fig. 1b: Hydrolyse de la liaison peptidique

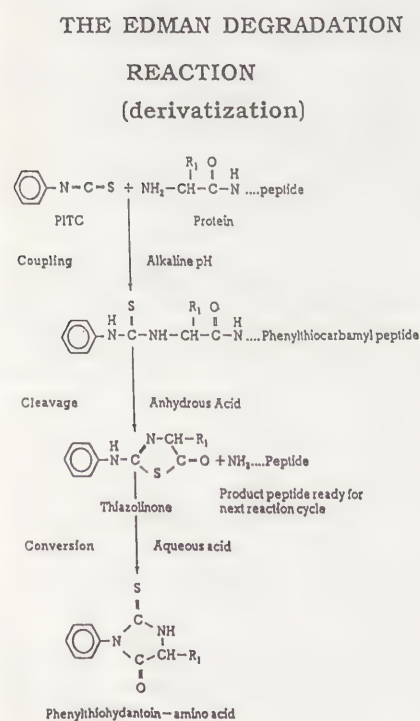


Fig. 2a: La réaction d'Edman

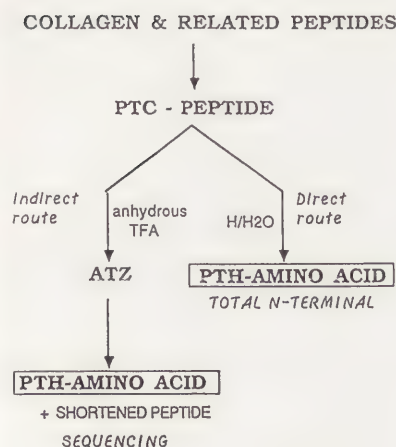


Fig. 2b: Les 2 voies d'obtention des dérivés PTH

2—le clivage se produit en présence d'acide anhydre qui provoque une cyclisation du dérivé PTC et produit une anilinothiazolinone (ATZ) correspondant à l'acide aminé N-terminal original et un peptide écourté par la perte de son résidu N-terminal et prêt pour un nouveau couplage éventuel. L'ATZ est séparé du peptide par extraction dans un solvant hydrophobe.

3—la conversion de la thiazolinone instable en un dérivé PTH plus stable est accomplie par un simple traitement en milieu acide dilué.

La description de toutes ces étapes permet de mieux comprendre les réactions qui se produisent en particulier celle du clivage qui exige d'être effectué en milieu acide anhydre afin de préserver le reste de la molécule pour une autre réaction en vue de sa détermination séquentielle. Ceci n'est pas nécessaire pour notre analyse.

Ilse et Edman [6] mentionnent qu'il est possible de combiner les étapes du clivage et de la conversion: la simple action d'un acide en milieu aqueux sur le phénylthiocarbonyl-peptide permet de libérer directement le dérivé PTH du résidu N-terminal mais provoque également l'hydrolyse du reste de la chaîne peptidique. L'obtention du PTH est possible mais la réaction n'est pas nécessairement reproductible et quantitative. De leur côté, Jenö et Chang [7] présentent deux voies d'accès aux dérivés DABTH à partir du DABITC, un composé structuralement très proche du PITC: l'une directe avec l'action d'acide dilué en milieu aqueux (H^+/H_2O) qui est utilisée dans l'Analyse Quantitative des N-terminaux (QNA) [3], l'autre indirecte mettant en oeuvre toutes les étapes de la dégradation d'Edman (voir Fig. 2b). Les deux voies seront éprouvées.

Expérimentation

Préparation des échantillons

On dispose de cuirs de veau neufs vieilliss artificiellement et d'un cuir ancien (ou historique). En raison de la modicité des prises d'essai, il n'a pas été possible de les broyer dans notre type d'installation. Les cuirs ont été découpés finement aux ciseaux et écrasés dans un mortier lorsque cela était possible.

L'un des problèmes majeurs dans l'étude du cuir est certainement la difficulté de le mettre en solution avec un minimum de dégradation; l'accès du réactif aux différents sites réactionnels est d'autant facilité que la protéine est solubilisée. Il existe plusieurs solvants capables de dissoudre plus ou moins les protéines. Parmi eux, on trouve le N, N-diméthylformamide (DMF), l'acide formique, l'acide trifluoroacétique (TFA) pur à température ordinaire qui ne provoque pas d'hydrolyse, ou encore plus spécifiquement pour le collagène de l'acide acétique 0,1 N ou 0,5 N à froid. Cependant nous utiliserons le milieu de couplage de la réaction d'Edman comme milieu de "solubilisation". Des essais préliminaires ont montré que le mélange d'eau et de pyridine à volume égal était assez efficace: on obtient une dissolution quasi immédiate du collagène pur et des cuirs en 24 h à 72 h. Une élévation de température favorise ce phénomène mais peut engendrer des réactions de dégradation surtout pour les cuirs fragilisés.

Dans la présente étude, tous les cuirs ont été traités dans les mêmes conditions expérimentales. On ajoute 3 ml du mélange eau-pyridine (1:1, v/v) à une prise d'essai de 0,1 g de cuir broyé ou finement coupé en morceaux. Le tout est enfermé, sous un balayage d'azote, dans un tube et mis en agitation à 30°C pendant 24 h dans un bloc chauffant.

Alors que le cuir ancien se dissout assez rapidement, les autres cuirs sont encore présents sous la forme de particules gonflées mais pas totalement dissoutes au bout de 24 h. Cela laisse à penser que plus le cuir est dans un état de dégradation avancé, meilleure est sa mise en solution. De même, il est à noter qu'un broyage fin est un facteur facilitant cette opération.

Mode opératoire pour la "dérivation"

Bien que la réaction d'Edman soit réalisée couramment par des appareils automatiques spécialement conçus pour le séquençage des protéines, la dérivation manuelle en phase liquide est plus adaptée pour l'analyse des résidus N-terminaux.

La synthèse manuelle de dérivés phénylthiohydantoïnes est une succession de manipulations assez longues et surtout très délicates à mettre en oeuvre surtout lorsqu'il s'agit d'un matériau comme le cuir.

Le couplage s'effectue directement sur le cuir mis en solution (voir plus haut) en ajoutant 50 μ l de PITC. On laisse la réaction se développer pendant 20 min à 50°C. On extrait plusieurs fois les réactifs dans la phase organique par un mélange d'heptane et d'acétate d'éthyle (2/1, v/v). Après séchage de la phase aqueuse sous vide, on ajoute 1 ml d'acide chlorhydrique 3N et 1 ml d'acide acétique 1N. L'étape de clivage-conversion se fait alors à 45°C pendant 40 min.

Tous les dérivés PTH synthétisés sont extraits par l'acétate d'éthyle, à l'exclusion des PTH de l'histidine et de l'arginine qui demeurent dans la phase aqueuse. Ils sont ensuite séchés et conservés sous azote à -20°C en attendant l'analyse chromatographique. Dans cette étude, ne sont pris en compte que les PTH présents dans la phase organique.

Chromatographie liquide (CLHP)

En CLHP à polarité de phase inversée, les solutés sont élués par ordre de polarité décroissante. Meuth et Fox [8] ont proposé une séparation complète des PTH d'acides aminés en 15 minutes suivant un gradient linéaire de phase mobile, sur une colonne Altex Ultrasphere ODS (250 mm \times 4,6 mm, particules de 5 μ m avec des pores de 80 Å). La colonne est maintenue dans un four à une température constante de 50°C. La phase mobile est constituée de deux éluants:

- éluant A: solution aqueuse d'acétate d'ammonium 17 mM à pH 4,5/acéto-nitrile (9:1, v/v)
- éluant B: même mélange mais avec une répartition inversée (1:9, v/v)

Temps (min)	Débit (ml min ⁻¹)	Composition de la phase mobile		
		A (%)	B (%)	Durée (min)
conditions initiales	1	70	30	—
0	1	70	30	0
1	1	50	50	3
12	1	70	30	1
20				

On peut suivre sur chaque chromatogramme la courbe représentant la composition de la phase mobile au cours de la séparation.

Les analyses sont effectuées sur un chromatographe HPLC (Beckman) muni de 2 pompes, commandé par le "Gold system" (Beckman), avec un détecteur UV (Spectra 100) réglé à 269 nm qui correspond à la longueur d'onde d'absorption maximale des PTH d'acides aminés.

Les produits obtenus après réaction au PITC sont redissous dans un mélange d'eau et d'acétonitrile (2:1, v/v) afin d'être chromatographiés. Les PTH d'acides aminés sont reconnus grâce à une table d'identification des dérivés PTH établie précédemment à partir de temps de rétention obtenus sur des séries de mélanges étalons. On peut même confirmer la nature des pics par co-injections de solutions étalons. Une calibration est nécessaire pour l'analyse quantitative. Elle est réalisée avec des solutions de mélanges étalons de PTH sur une gamme de concentrations bien déterminées.

Analyse des cuirs

Des essais préliminaires nous ont conduits à énoncer quelques considérations générales sur l'analyse des PTH sur des cuirs. Tout d'abord, c'est la méthode directe qui a été choisie pour la fabrication des dérivés PTH à partir des échantillons de cuir car elle présente le grand avantage d'alléger le mode opératoire, donc de diminuer les pertes, sans affecter les résultats par rapport à la voie indirecte.

L'identification des pics correspondant à des PTH d'acides aminés peut être gênée par la présence de nombreux autres pics présents sur le chromatogramme

et dûs pour la plupart à des sous-produits de réaction. C'est le cas notamment pour la phénylalanine, et surtout pour la lysine complètement masquée par la présence d'un énorme pic saturé de ce qui semble être de la phénylthiourée (PTU). Ce produit éluant à un temps de rétention de 9,40–9,50 minutes, juste après la diphénylthiourée (DPTU), serait formé par le PITC en présence d'ammoniac. On remarque également que pour certains cuirs, il est très difficile, voire impossible d'identifier les éventuels dérivés PTH éluant à des temps de rétention compris entre 1,8 et environ 3 minutes, en raison de la présence d'une multitude de pics correspondant sans aucun doute à des produits polaires contenus dans le cuir (ni le témoin de réaction ni le collagène ne présentent ce type de phénomène).

Des peaux de veau tannées de deux manières, les unes au sumac (tanin hydrolysable) et les autres au mimosa (tanin condensé), ont été soumises à la pollution atmosphérique simulée dans un caisson expérimental parallèlement au British Leather Centre (BLC) à Northampton [9] et au Centre de Recherches sur la Conservation des Documents Graphiques (CRCDG) à Paris [10]. Les échantillons prélevés au bout de plusieurs semaines sont analysés et comparés à leurs témoins respectifs non vieillis. Les échantillons MA₁ et MA₂, tannés au mimosa et vieillis au CRCDG n'ont pas encore été analysés. Cependant ils se présentent dans un état physique satisfaisant (ne se déchirent pas à la main) bien que leur couleur ait commencé à virer sur une teinte plus rouge.

Le cuir ancien (échantillon 11 H) est prélevé à partir du cuir de revêtement d'un coffre datant du 17^{ème} siècle. L'analyse porte sur le côté chair du cuir dont la structure fibreuse est lâche et fragile. Une analyse de tanins a montré qu'il s'agissait certainement de tanins de type condensé [11].

Résultats

Les cuirs de veau tannés au sumac (témoin, SA₁ SA₂ et 12R₃):

Les résultats montrent explicitement que le traitement mené au BLC (échantillon 12R₃) a été beaucoup plus drastique que celui du CRCDG (échantillons SA₁ et SA₂).

Dans les cuirs vieillis au CRCDG on a une prépondérance de Ala par rapport à Gly en tant que N-terminal. L'échantillon 12R₃ se distingue notamment par une quantité importante de sérine. (voir Fig. 3)

Les cuirs de veau tannés au mimosa (témoin, 12R₄):

De visu, l'échantillon prélevé au BLC (12R₄) se trouve dans un état de dégradation très poussé. Il se déchire facilement à la main, sa couleur a viré au rouge ce qui est tout à fait caractéristique des cuirs à tanins condensés. (voir Fig. 4)

Le chromatogramme du cuir ancien présente de nombreux pics (voir Fig. 5) dont la majeure partie correspond à des dérivés PTH d'acides aminés. L'identification et la quantification sont plus aisées que dans le cas de cuirs neufs ou vieillis artificiellement. On retrouve à peu près tous les PTH des acides aminés constitutifs du collagène. On remarque une forte proportion de PTH-Ala, de PTH-Ser, de PTH-Gly, de PTH-Hyp, de PTH-Pro, PTH-Thr; les autres étant présents à des concentrations plus faibles.

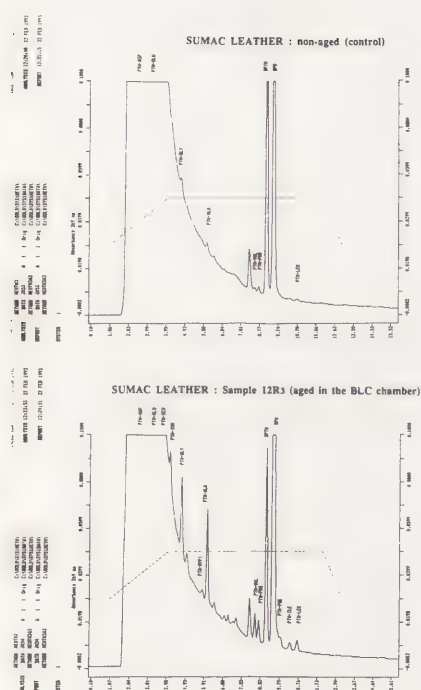


Fig. 3.

←
Fig. 3: Chromatogrammes des dérivés PTH obtenus sur un cuir de veau tanné au sumac (dilué au 1/10 par rapport aux autres injections) (les temps de rétention sont exprimés en minutes)

témoin (avant vieillissement)

temps de rétention	3,45	4,71	6,05	8,72	9,12	9,47	9,88	10,69
dérivé PTH	PTU	Gly	Ala	Pro	DPTU	DPU	Phe	Leu

vieilli au BLC

temps de rétention	3,45	3,76	4,12	4,72	5,80	6,05	8,72	9,12	9,47	9,83	10,31	10,68
dérivé PTH	PTU	Ser	Thr	Gly	Hyp1	Ala	Pro	DPTU	DPU	Phe	Ile	Leu

Les valeurs de résidus N-terminaux obtenues en analyse quantitative sont consignées dans le tableau général suivant (en $\mu\text{mol./g}$ de cuir). Les pics mal intégrés sont notés "m.i."

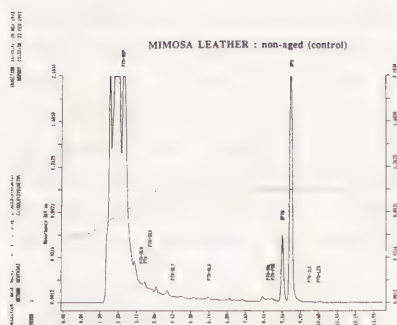


Fig. 4: Chromatogrammes des dérivés PTH obtenus sur un cuir de veau tanné au mimosa

témoin

temps de rétention	3,32	3,47	3,75	4,08	4,72	5,77	6,12	8,74	9,16	9,49	10,36	10,74
dérivé PTH	Glu	PTU	Ser	Thr	Gly	Hyp1	Ala	Pro	DPTU	DPU	Ile	Leu

vieilli au BLC

temps de rétention	3,33	3,48	3,79	4,17	4,76	5,36	5,85	6,09	8,78	9,18	9,47	9,91	10,39	10,77
dérivé PTH	Glu	PTU	Ser	Thr	Gly	Hyp2	Hyp1	Ala	Pro	DPTU	DPU	Phe	Ile	Leu

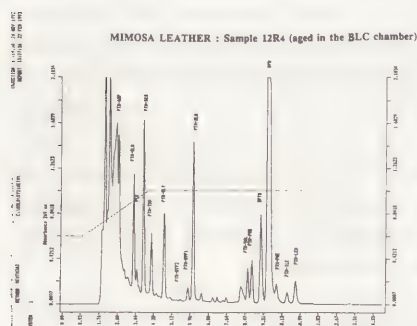


Fig. 4.

Fig. 5: Chromatogramme des dérivés obtenus sur un cuir ancien (temps de rétention en minutes)

temps de rétention	3,31	3,47	3,77	4,14	4,74	5,30	5,82	6,06	8,74	9,15	9,49	9,87
dérivé PTH	Glu	PTU	Ser	Thr	Gly	Hyp2	Hyp1	Ala	Pro	DPTU	DPU	Phe

temps de rétention	10,34	10,73
dérivé PTH	Ile	Leu

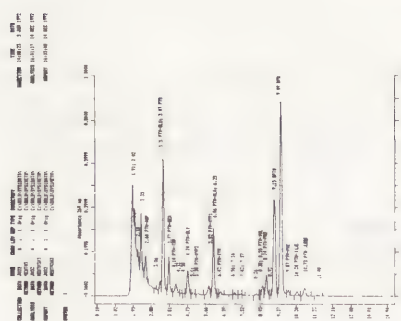


Fig. 5.

PTH	Sumac		Mimosa		Cuir ancien
	Témoin	Vieilli	Témoin	Vieilli	
		BLC	BLC	BLC	
Asp	m.i.		m.i.	m.i.	2,05
Glu	1,22(?)	1,21	<0,01	1,07	0,33
Ser	—	0,61	<0,01	2,59	2,36
Thr	—	0,11	<0,01	1,48	1,24
Gly	0,07	0,46	?<0,01	1,00	1,55
Hyp2	—	—	—	—	0,32
Hyp1	—	0,08	0,01	0,29	1,29
Ala	0,03	0,58	0,03	1,93	4,38
Tyr	0,03	0,06	0,01	—	0,18
Met	—	0,25?	—	—	—
Val	0,03	0,12		0,29	0,46
Pro	0,03	0,11		0,50	1,25
Phe	0,01	0,03			0,25
Ile	—	0,07	<0,01	0,15	0,32
Leu	0,02	0,11	0,01	0,40	0,69

Remarque: PTH-Asp et PTH-Glu, à un degré moindre, n'ont pas pu être déterminés avec précision en raison de la multitude de pics présents dans cette partie des chromatogrammes. PTH-Hyp apparaît normalement sous forme d'un seul pic PTH-Hyp1. Mais il s'accompagne parfois d'un autre pic PTH-Hyp2 éluant un peu avant.

D'une manière générale, on constate une augmentation globale des résidus N-terminaux dans l'échantillon de cuir ancien et de cuir vieilli artificiellement à la pollution par rapport à un cuir non vieilli. L'importance relative de chaque type de résidus N-terminaux est modifiée suivant les cas. On note étrangement un accroissement considérable de la quantité de PTH sérine dans les échantillons vieillis naturellement et artificiellement.

Discussion

Evolution du nombre de N-terminaux en fonction du vieillissement:

Pour les 2 types de cuir (sumac et mimosa), le vieillissement artificiel a induit un accroissement sensible des groupements N-Terminaux qui permet d'apprécier l'étendue de la dégradation hydrolytique occasionnée par les polluants, surtout dans les conditions fixées au BLC.

Contribution des différents acides aminés au N-terminal:

On ne considère que les dérivés majoritaires c'est à dire ceux de Gly, Pro, Ala, Hyp, Thr et Ser. Après avoir rapporté leurs concentrations relatives en % de mol., on compare avec la répartition des acides aminés dans le collagène donnée par l'analyse des acides aminés (AAA) des témoins pour les cuirs vieillis et de l'échantillon lui-même pour le cuir historique [11].

Les valeurs retenues sont celles des échantillons vieillis au BLC car elles sont plus élevées. (On notera entre parenthèses le classement des dérivés PTH par ordre d'importance numérique.)

PTH	Sumac			Mimosa			Cuir 11 H	
	Témoin	Vieilli	AAA	Témoin	Vieilli	AAA	N-terminal	AAA
Gly	(1)	23,59 (3)	46,90 (1)	<0,01	12,84 (4)	47,06 (1)	12,84 (3)	48,44 (1)
Pro	(2)	5,64 (4)	17,46 (2)	m.i.	6,42 (5)	17,39 (2)	10,35 (5)	17,01 (2)
Ala	(2)	29,74 (2)	15,37 (3)	0,03 (1)	24,77 (2)	15,42 (3)	36,29 (1)	15,56 (3)
Hyp	—	4,10 (6)	13,28 (4)	0,01	3,72 (6)	13,27 (4)	10,69 (4)	12,32 (4)
Ser	—	31,28 (1)	4,55 (5)	<0,01	33,25 (1)	4,48 (5)	19,55 (2)	4,29 (5)
Thr	—	5,64 (4)	2,44 (6)	<0,01	19,00 (3)	2,37 (6)	10,27 (6)	2,37 (6)

A supposer que les risques de coupures de chaîne soient statistiquement équivalents pour toutes les liaisons peptidiques, la proportion de résidus N-terminaux pour un acide aminé devrait correspondre avec celle de son importance relative au sein de la molécule.

Alors que dans les témoins sumac et mimosa, les contributions, même modestes, de la glycine, de la proline et de l'alanine sont logiques du fait de leur importance numérique au sein de la molécule de collagène, dans le cas des échantillons pollués, c'est la sérine et l'alanine qui contribuent le plus aux résidus N-terminaux contrairement à ce que l'on pouvait attendre. L'hydroxyproline PTH est pratiquement absente du témoin et demeure très discrète dans les échantillons vieillis.

Quant au cuir ancien, les proportions relatives des différents PTH ne correspondent pas du tout à celles de sa composition en acides aminés du collagène. On s'aperçoit que la contribution de la glycine, de la proline et de l'hydroxyproline en tant que résidu N-terminal est particulièrement faible compte tenu de leur fréquence dans la molécule. Par contre, celle de l'alanine, de la sérine et de la thréonine est particulièrement importante.

Conclusion

La méthode doit être affinée afin de permettre l'identification des quelques PTH masqués par les sous-produits de réaction. Elle devra s'étendre à l'analyse des éventuels PTH de l'histidine, de l'arginine et de l'hydroxylysine. L'abondance surprenante de la sérine en tant que résidu N-terminal mérite d'être confirmée par une identification structurale en couplage avec la spectrométrie de masse.

Remerciements

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Produits

La pyridine de qualité HPLC/Spectro grade et le PITC ainsi que tous les étalons de PTH d'acides aminés proviennent de PIERCE Europe, POB 1512, 3260 BA Oud-Beijerland, Pays Bas.

Les acides utilisés pour le clivage-conversion et le n-heptane Chromanorm sont produits par PROLABO France, 65, Bd Richard Lenoir, 65011 Paris, France.

Le méthanol, l'acétonitrile et l'acétate d'éthyle sont de qualité Lichrosolv pour la chromatographie et sont achetés chez MERCK-CLEVENOT, Division Réactifs, 5-9 rue Anquetil, 94736 Nogent sur Marne, France.

L'eau est de qualité HPLC.

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Abstract

The tannins extractable from new and aged leathers in a water/acetone solution (1/1, v/v), were measured by high-performance liquid chromatography (HPLC) and expressed as the integrated absorption of all tannin peaks at 280 nm, or as gallic acid equivalents per 100 mg of dry leather. Colorimetric analysis of the extracts for the presence of phenolic substances was given as an amount of gallic acid equivalents per 100 mg of dry leather. These analytical data showed that the tannin content of leathers without the need for other analyses; also, the tannin type (hydrolysable or condensed) does not have to be determined for new leathers. Parameters such as the HPLC elution profile, the spectral characterisation of individual peaks or fractions, and the calculation of the relative abundance of ellagic acid, protocatechuic acid and other small molecules were combined to identify the tannin types of historical leathers. The changes in the tannin profile brought about by both artificial and natural ageing of leather were also evaluated.

Keywords

Leather, tannins, vegetable, chromatography, high-performance liquid chromatography (HPLC)

High-Performance Liquid Chromatography of Vegetable Tannins Extracted from New and Old Leather

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Introduction

The amount of vegetable tannins extracted from leather is described in such normalised procedures as the "degree of tannage" (Indice de tannage). This value must be calculated from other analytical data obtained from the leather sample, such as: weight of conditioned leather, volatile matter, oils and fats, hide substances, organic water solubles, and total ash. Hence, as approximately ten grams of leather are required to determine the amount of bound organic matter, each calculation involves inherent deviations. Moreover, the degree of tannage is a figure which only describes what proportion of the hide substance of the conditioned leather sample might be tannins. This figure does not yield any further information on the nature and the condition of the (vegetable) tannins or any other hide-bound organic substances present. Other methods are available to determine the amount of tannins in extracts by ultraviolet and visible spectrometry (1-4). The fractionation of tannin samples into several groups and the description of methods identifying some individual tannin components have been described before (5-6).

The present paper describes the application of a chromatographic method to the analysis of tannins extracted from leather. This method allows the separation and characterisation of individual tannin components and the calculation of the amount of extractable tannin without the need to determine other analytical parameters except volatile matter. On the other hand, this way of tannin quantification may be incorporated into a complete scheme for leather analysis. This scheme can be performed using leather samples as small as 200 mg, and comprises tests for shrinkage temperature, volatile matter, pH, anions, tannins, oils and fats, and minerals (7).

Sample preparation

Tannins may be extracted from leather either directly if only the tannin analysis must be performed, or after preliminary extraction of water soluble materials if a more complete analysis is required. In the latter case, only a minute amount of the preliminary aqueous extract is used for determinations of pH and anions. As the aqueous phase is recovered for more than 95%, even small amounts of extracted tannins it will not be lost.

As described in the literature, tannin extractions for leather clippings were performed in a water/acetone (1/1, v/v) solution in closed vessels at room temperature for 24 hours (8). The volume of extracting liquid was 100 ml per gram of climatised leather. The leather was weighed after conditioning for at least 48 hrs at 65% relative humidity and 20°C. In the case where the leather had been formerly extracted in water, acetone was added to the aqueous extract remaining after sampling to reach a 1/1 volumetric ratio. Just before chromatography, an appropriate sample of the water/acetone extract was diluted five-fold with methyl alcohol. Extracts were frozen at -20°C when analyses could not be performed immediately.

Analytical procedures

The chromatographic conditions were as follows: column Spherisorb ODS2, 3 µm, 100 × 4.6 mm (Alltech, Laarne, Belgium); pump HP-1050 (Hewlett-Packard, USA); 990+ photodiode-array detector (Waters-Millipore, USA); data-handling NEC APCIV computer and Waters 5200 printer plotter (Waters-Millipore, USA); 20 µl sample loop; flow rate: 1.2 ml/min; analytical wavelength 280 nm (other post-run selections possible between 200 and 800 nm); flow

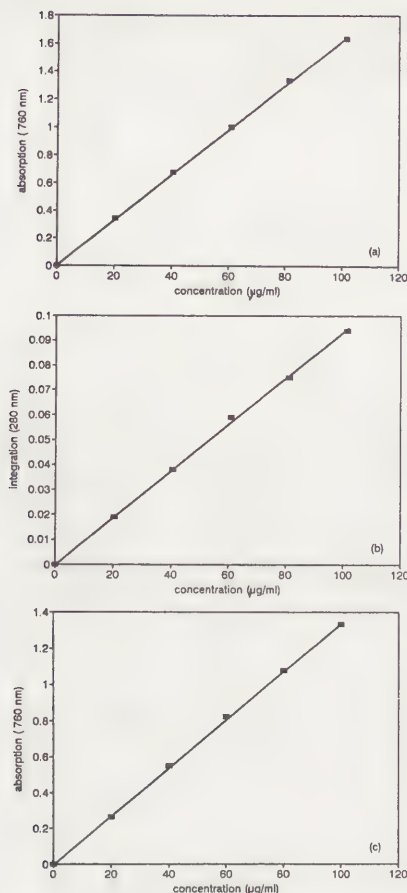


Figure 1: calibration graph for the calculation of the concentration of gallic acid in solution with colorimetry (a) or HPLC (b), and of catechin with colorimetry (c).

scheme (A = methanol, B = water, C = 50 g/l phosphoric acid in water): 10A/80B/10C for 2 min, linear gradient to 90A/10C during 17 min, 90A/10C for 3 min; temperature 21°C.

The total amount of extractable tannin was calculated from the HPLC chromatogram by integrating all the tannin peaks in the chromatogram at 280 nm and by expressing this integration in either of the following ways. OD280/100mg was the optical density that would be obtained if 100 mg of dry leather were extracted with 1 ml of water/acetone (1/1, v/v) solution. GAeq/100mg(HPLC) was the amount of gallic acid equivalents in mg, present in 100 mg of dry leather and was calculated with the help of a calibration curve giving the relation between the concentration of gallic acid injected and its integration at 280 nm (See fig. 1a). Taking into account an injected volume of 20 µl, a five-fold dilution of the extract before injection, an integration value of A280, an amount of M mg leather extracted, an extraction volume of V ml, and an integration of 0.094 at 280 nm for 100 µg/ml of gallic acid, the calculation of the OD280/100mg followed from the formula: $25000 \cdot A_{280} \cdot V / M$, and that of GAeq/100mg(HPLC) from: $532 \cdot A_{280} \cdot V / M$. Examples of analysis and calculation of tannins extracted from a new sumac or mimosa leather are given in figures 2a and 2c and in table 1 (9).

Table 1. Calculation of tannins extracted from new mimosa and sumac tanned leathers.

	Mimosa	Sumac
Amount of dry leather (mg)	719	730
Volume of extract (ml)	63	61
HPLC integration (280 nm)	0.130	0.681
OD280/100 mg	290	1400
GAeq/100 mg (HPLC)	6.1	36
GAeq/100 mg (COL)	19	26
(OD280/100 mg)/(GAeq/100 mg (COL))	15	54

Each HPLC chromatogram may be unraveled further by looking at the spectral characteristics of each tannin peak, leading to the recognition of small (monomeric) molecules, e.g., gallic acid, protocatechuic acid, catechin and ellagic acid (See fig. 3a–3d) and to the description of other peaks or fractions as to spectrally resemble the formerly-cited monomers (See fig. 2a–2f). These considerations may be helpful for the determination if the tannin type was condensed or hydrolysable (10).

The amount of extractable tannins was also evaluated by colorimetry of phenolic substances, not only as a measurement to be considered alone, but also to be compared with quantitative HPLC results (3). The colorimetric measurements were expressed as the amount of gallic acid equivalents per 100 mg of dry leather (GAeq/100mg(COL)) by means of a calibration curve for gallic acid (See fig. 1b). These results are outlined in Table 1.

Evaluation of analytical results

The analytical data from Table 1 show comparable figures for the tannin content of sumac leather, calculated as either GAeq/100mg(HPLC) or GAeq/100mg(COL). There is no match, however, for the mimosa tanned leather for the following reasons: the tannin components in mimosa are based on catechin and not on gallic acid; the colorimetric calibration curve for catechin is lower than that for gallic acid (See fig. 1c); the molar extinction coefficient at 280 nm for catechin is 2.4-fold lower as compared to gallic acid. It was preferred to keep to gallic acid as reference product, also for mimosa tanned leather because it is exactly this kind of "match and mismatch" could be helpful in identifying tannin types of new leathers as hydrolysable (gallic acid) or condensed (catechin). The ratio that will be used for this criterion is (OD280/100mg)/(GAeq/100mg(COL)), as indicated in the last row of table 1.

When the sumac tannin was considered to be mainly penta-galloyl-glucose (molecular mass = 940), then the amount in gallic acid equivalents (molecular

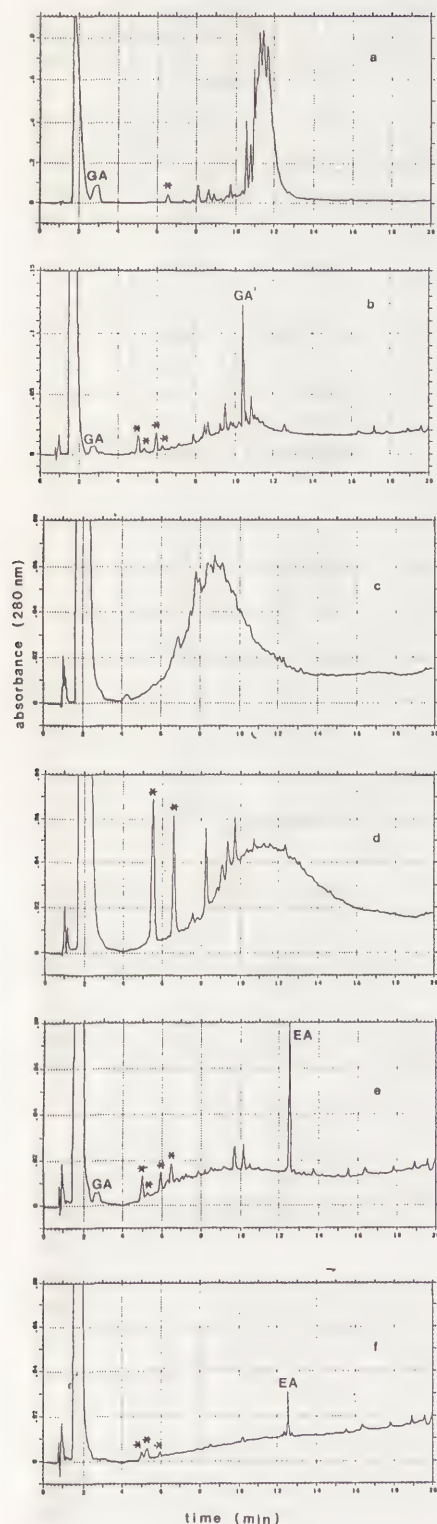


Figure 2: HPLC elution profile of tannin extracted from new and aged leather; (a): new sumac: S-0 (See table 2); (b): historical leather 4 (See table 3); (c): new mimosa: M-0 (See table 2); (d): short-term aged condensed tannin: CT2-1 (See table 2); (e): historical leather 10 (See table 3); (f): historical leather 5 (See table 3); GA: gallic acid; GA': peak with gallic acid spectral characteristics; PCA: protocatechuic acid, EA: ellagic acid, (*) belonging to "M" in tables 2 and 3; horizontal bars indicate the fractions incorporated in tannin integration.

mass = 170) might be recalculated to give 40 or 29 mg of tannin per 100 mg of dry leather, from HPLC or colorimetry, respectively (11). These figures are close to the 34.8% of bound organic matter obtained with conventional methods (12).

An initial series of analyses was performed on leathers with known types of tannage and ageing history (reference leathers). S-0 and S-1 were sumach tanned leathers, M-0 and M-1 were mimosa tanned leathers, and S-0 and M-0 were unaged reference samples. The ageing of S-1 and M-1 was carried out in a polluted atmosphere (SO₂, NO₂, NO, 40°C, 20%RH), as described in the literature (12). CT1-0, CT1-1, CT2-0 and CT2-1 were leathers tanned with condensed tannins of unknown origin. CT1-0 and CT2-0 were kept for 10 years in a laboratory environment (23°C, 50% RH, darkness); CT1-1 was exposed in a basement storage room, located along a street with traffic, for 10 years; CT2-1 was exposed in a reading room close to a window, also for ten years (13). The analytical results are given in table 2; some HPLC elution profiles are shown in figure 2.

Table 2. Extractable tannin from unaged and aged reference leathers; S: sumac; M: mimosa; CT: condensed tannin; "-0": unaged; "-1": aged; ageing conditions described in the text; figures were calculated from HPLC analysis (OD280/100 mg) or colorimetry (GAeq/100 mg (COL)); GA: gallic acid, EA: ellagic acid, M: monomers; R: ratio (OD280/100 mg)/(GAeq/100 mg (COL)).

Leather	OD280/100 mg				GAeq/100 mg (COL)	R
	Total	GA	EA	M (%)	total	
S-0	1580	70	2.2	10 (1)	26	61
S-1	1480	44	9	11 (1)	26	57
M-0	365	1	0.1	0 (0)	19	19
M-1	260	1	0.2	2 (1)	13	20
CT1-0	328	0.3	0	8 (2)	19	17
CT1-1	339	0.3	0	22 (6)	18	19
CT2-0	410	0.8	0	7 (2)	21	20
CT2-1	504	0.5	0	33 (7)	17	30

The 20 historical calf skin leathers used in the analysis ranged in age from the early 16th to the late 19th century (14). The analytical results are given in table 3, and some HPLC elution profiles are shown in figure 2.

Generally, the HPLC elution profile was less characteristic for aged samples, and the presence of monomers (M) became more prominent (See figs. 2c, 2d and 2f). The increased abundance of monomers (M) in tannin extracts from aged samples was most clearly seen when relative ratios were considered (figures between brackets in tables 2 and 3). This relative increase might be ascribed to the concurrent decrease of total extractable tannin in historical samples (compare total OD280/100 mg in tables 2 and 3). In short-term naturally aged samples however, an absolute increase in M content also occurred (compare M as OD280/100 mg and % M in CT-samples from Table 2). The calculation of %M in total extractable tannin might be put forward as a parameter to measure leather ageing. In future research the evolution of this parameter should be evaluated in relation to other parameters, such as the amino acid composition of the hide substance and the number and amounts of amino acid end groups.

The ratio (OD280/100mg)/(GAeq/100mg(COL)) was indicative of the tannin type of new and artificially aged leathers. For hydrolysable tannins, figures between 54 and 61 have been obtained so far; for condensed tannins the range was 15 to 30 (See tables 1-2). Obviously, this ratio was no longer useful to derive the tannin type of naturally aged historical leathers (See table 3). The condensed type of tannin present in the CT-leathers of table 2, as indicated by the ratio, was confirmed by the HPLC elution profile (See fig. 2d) and spectral analysis.

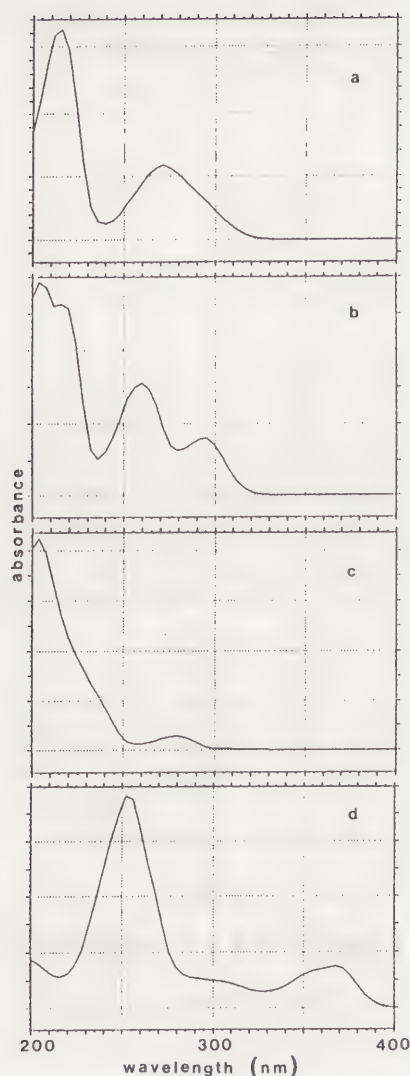


Figure 3: spectral characterisation of individual tannin peaks and fractions; (a): gallic acid; (b): protocathechuic acid; (c): catechin; (d): ellagic acid.

Table 3. Extractable tannin from historical leathers (14); calculation of figures and abbreviations as in Table 2; TT: tannin type; H: hydrolysable; C: condensed; HG: hydrolysable gallotannin.

Leather (age)	TT	OD280/100 mg				GAeq/100 mg (COL) total	R
		Total	GA	EA	M (%)		
1 (1838)	H	62	0.3	3.9	2.6 (4)	1.9	33
2 (1882)	HG	104	0.1	0.3	14 (13)	4.3	24
3 (19c)	C	255	0.2	0.1	16 (6)	12.3	21
4 (19c)	HG	211	3.8	1.9	11 (5)	9.6	22
5 (1700-'30)	H	44	0.5	3.7	3.8 (9)	1.9	23
6 (—)	H	108	0.9	7.2	5.4 (5)	2.6	42
7 (18c)	H	150	0.8	11	10 (7)	4.5	33
8 (c.1550)	H	147	0.5	5.6	6.7 (5)	3.2	46
9 (18c)	H	140	1.1	9.0	10 (7)	4.4	32
10 (—)	H	170	3.1	14	6.5 (4)	7.7	22
11 (c.1600)	C	117	0.7	0.2	5.2 (4)	4.4	27
12 (18c)	H	59	0.5	6.1	4.8 (8)	3.1	19
13 (c.1730)	H	74	0.7	5.3	6.5 (9)	4.3	17
14 (c.1830)	H	96	0.2	7.7	2.6 (3)	3.5	27
15 (c.1890)	HG	176	1.8	8.4	10 (6)	9.2	19
16 (18c.)	H	53	0.3	6.2	3.7 (7)	2.2	24
17 (1850)	H	186	1.5	8.6	5.2 (3)	7.0	27
18 (1710-'40)	H	28	0.2	3.5	0.6 (2)	1.2	23
19 (1880)	H	45	0.4	1.9	2.9 (6)	1.0	45
20 (1700)	H	19	0.1	1.5	1.3 (7)	0.7	27

In 16 of the 20 historical samples, ellagic acid (EA) was the most prominent single component present. In all these cases, no specific elution profile remained (See fig. 2f). It may be dangerous to postulate that the presence of ellagic acid excludes the use of condensed tannins, since small amounts of ellagic acid were clearly demonstrated in mimosa tanned leather after ageing (See M-1 in table 2), as well as in the original mimosa tanning material. In future research, this phenomenon should be carefully followed.

The most probable type of tannin of the historical leathers in table 3 was determined according to the following criteria: the lack of or few multiple peaks with gallic acid and/or ellagic acid spectral characteristics point to condensed tannins (C). When multiple distinct peaks occur which show spectral characteristics that conform to gallic acid, these most probably represent hydrolysable gallotannins (HG; see fig. 2b). HPLC chromatograms with prominent amounts of ellagic acid were considered to be hydrolysable tannins (H) without any further specification. It is emphasized that this classification is preliminary and based upon, for the time being, uncertain criteria.

When considering the data on general elution profile, total amount of extractable tannins (OD280/100 mg), %M, the ratio (OD280/100mg)/(GAeq/100mg(COL)), and abundance of ellagic acid, it might be concluded that the changes which occurred in the levels of extractable tannins of artificially aged leathers do not conform to what happened upon long-term and even short-term natural ageing. In order to simulate long-term natural ageing, the ageing parameters should be modified, probably to allow more oxidative breakdown (12).

Conclusions

High-performance liquid chromatography of extractable tannins may be used to calculate the amount of vegetable tannins present in leather. This approach only involves the determination of the weight of the leather sample in its climatized and dried condition.

The HPLC elution profiles and the spectral analyses of chromatographic peaks and fractions, obtained from both new, artificially- and naturally aged leathers give important data for the recognition of the tannin type and for the estimation of the tannin (or leather) degradation.

This kind of analysis requires only 10 mg of leather, if the weight of the climatised leather is taken as the reference for calculations. Tannin analysis may be performed within the context of a scheme for total leather analysis with as little as 200 mg of leather.

Acknowledgements

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Working Group 19

Easel Paintings on Rigid Support

Peintures de chevalet sur supports rigides



Résumé

Cette communication porte sur la restauration d'un "trompe-l'oeil chantourné", transformé et défiguré lors d'une restauration antérieure. Il représente en grandeur nature une fillette endormie dans sa chaise haute. L'examen préliminaire à la restauration a révélé la présence d'un panneau en chêne chantourné encastré dans un support en sapin et habilement masqué par un épais vernis brunâtre sur la face et un lourd parquetage au revers.

L'état précaire du panneau fortement aminci (parquetage épais et fort lourd, déformation du bois, joints et fissures ouverts) ainsi que la qualité picturale médiocre du fond brun, contrastant avec la facture minutieuse et la palette chatoyante de la composition centrale nous ont amené à dégager le format original de l'oeuvre en supprimant la parquetage bloqué et les ajouts en sapin.

Ainsi renaissait un merveilleux trompe-l'oeil chantourné hollandais du XVII^e siècle.

Mots-Clés

Portrait d'enfant, trompe-l'oeil chantourné, dummy board figure, support, parquetage, rayons X, joints, fissures, armature en aluminium, J. Verspronck



Fig. 1 J. VERSPRONCK, *Enfant endormi*. (Coll. privé, Belgique) Le tableau rectangulaire avant restauration.

La restauration d'un trompe-l'oeil chantourné *Enfant endormi* peint par Johannes Verspronck en 1652

Betsy de Ghellinck d'Elseghem

Restauratrice de tableaux

Professeur, Atelier de restauration de peintures

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Introduction

En entrant dans l'atelier le tableau était de forme rectangulaire, mesurant 75,7 cm de largeur et 96 cm de hauteur (Voir fig. 1).

L'artiste a peint un jeune enfant, assis dans une chaise haute, qui s'est assoupi en mangeant sa panade. La cuillère, en tombant sur la tablette, a fait gicler la bouillie. Cet enfant n'est pas particulièrement calme: il a perdu un soulier et des traces de coups de pieds sont visibles en plusieurs endroits sur le battant de la porte ouverte. Dans le bas de la chaise, il y a un pot en terre cuite contenant des braises rougeoyantes: elles réchauffent les pieds de l'enfant à travers une tablette trouée. Un chat, recherchant la chaleur, se blottit contre la paroi de la chaise en faisant le gros dos.

Toute la surface picturale était recouverte d'un épais vernis brunâtre, qui modifiait fortement les valeurs chromatiques de l'oeuvre: les zones brunes étaient ternes et manquaient de profondeur, des détails nous échappaient. D'autre part, le vernis dissimulait habilement les restaurations antérieures telles que adjonctions, masticages et retouches.

Un premier examen à l'oeil nu révélait toute une série d'éléments suscitant des réflexions et questions, tant à la face qu'au revers:

—côté face:

- certaines planches sont larges et planes, d'autres étroites et ondulées;
- les joints sont discontinus;
- par endroits, il y a une légère dénivellation le long du contour de la chaise et du chat;
- il y a plusieurs incrustations de bois;
- les lattes ont été ajoutées le long des bords.

—côté revers (Voir fig. 2):

- dans les espaces laissés libres par les parquetages, on observe du bois de chêne, dont la structure est souvent discontinue;
- dans deux alvéoles, on rencontre du bois de sapin grossièrement teinté.

Ces observations ont été complétées par des examens au microscope, aux Rayons X, aux U.V. et aux I.R.¹. Les résultats nous ont permis de discerner les changements intervenus depuis la création de l'oeuvre, d'établir un diagnostic précis de l'état matériel et de retrouver l'aspect original du tableau. Finalement, ils nous guideront dans le choix d'une restauration adéquate, assurant la conservation du tableau d'une part et la restitution de sa fonction initiale de "trompe-l'oeil chantourné", d'autre part.

Technique picturale et état de conservation

Le support

Le tableau est peint sur un support en bois constitué de plusieurs planches verticales de largeur variable. Le revers est consolidé par un parquetage collé et fixe. Les radiographies (Voir fig. 3 et 4) ont révélé l'existence de deux types de bois différents dans le support: du chêne chantourné est encastré dans des éléments de sapin².



Fig. 2 Le parquetage au revers du tableau avant la restauration.

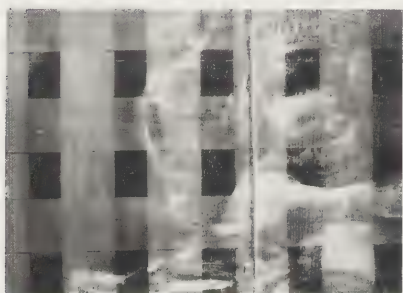


Fig. 3 Radiographie avant la restauration (Document du Lab.Art. U.C.L.).



Fig. 4 Radiographie avant la restauration (Document du Lab.Art. U.C.L.).

Technique picturale (Voir fig. 5)

a. *Le support en chêne = le support original*: il s'agit d'un panneau en chêne chantourné composé de trois éléments verticaux d'inégale largeur (de gauche à droite: 27,5 cm—26 cm—19 cm). La hauteur des planches varie selon la découpe supérieure. Ces éléments sont assemblés à rainure et languette et fixés à la colle d'os. Les planches sont débitées sur quartier. La tranche des contours est biseautée dans l'arrondi de la chaise et recouvert d'une fine couche de peinture noire; elle est droite dans la partie armoire et autour du chat. Dans le bas, le support se termine par une languette horizontale en chêne d'une largeur de 1,8 cm et d'une longueur variant de 68,4 à 69,3 cm. Cette latte servait vraisemblablement à protéger le bas du tableau, posé à même le sol.

b. *Le support en sapin = un support ajouté*. Ce support, appliqué vers la fin du XIX^e siècle par un restaurateur désirant commercialiser le tableau, sert à compléter les vides du chantourné pour en faire une surface rectangulaire. Il se compose de six planches verticales de largeur variable (gauche à droite: 11,4cm—13,4cm—13,5cm—14,7cm—13,5cm—7,5cm) dont le contour supérieur épouse la forme du chantourné. Trois lattes en sapin ont été collées respectivement sur la rive supérieure et les deux rives latérales.

Au revers, le sapin a été minutieusement dissimulé par des rectangles en chêne de 0,15cm d'épaisseur collés dans les surfaces non couvertes par le parquetage. L'ordre successif des rectangles n'a pas été respecté, d'où la discontinuité dans la texture du bois. D'autre part, deux espaces n'ont pas été recouverts: le sapin apparent a été grossièrement teinté (Voir fig 6).

c. *Le parquetage* (Voir fig.2,6). Un lourd parquetage en chêne a été apposé au revers du tableau rectangulaire pour en assurer la solidité. Les montants verticaux sont collés en surépaisseur sur le panneau. Les traverses, coulissantes à l'origine, se sont bloquées avec le temps.

Etat de conservation

Le support présente de nombreux dégâts et traces d'usure causés par de multiples manipulations et restaurations antérieures. (Voir fig.7).

a. *Le support en chêne*. Le tableau a été altéré par sa fonction première d'objet décoratif—un trompe-l'oeil chantourné posé à même le se sol—à la suite de

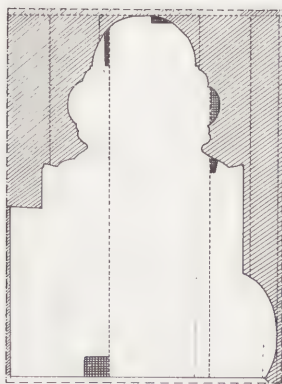


Fig. 5 Structure matérielle avant la restauration:

- contour du tableau rectangulaire
- contour du tableau chantourné
- - - - joint
- fissure
- chêne du support original
- ▨ sapin
- ▩ bois de chêne incrusté dans le tableau chantourné

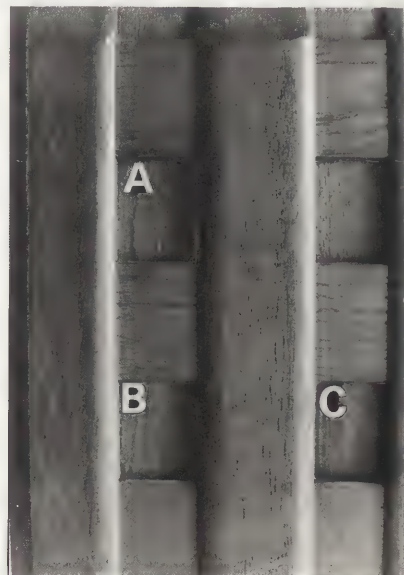


Fig. 6 Détail du coin supérieur gauche du revers. Un joint entre deux planches de sapin s'est ouvert.

A-B: la structure ligneuse du chêne est discontinue

C: bois de sapin teinté

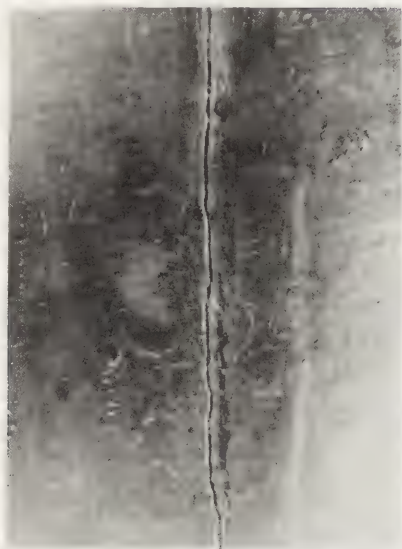


Fig. 7 Rupture du joint, côté face de fig. 6.



Fig. 8 Détail après le dévernissage, l'élimination des retouches et mastic anciens.



Fig. 9 L'ensemble après le dévernissage et l'élimination des retouches et mastic anciens. Les zones rabotées apparaissent. En bas, à droite, test de dévernissage du fond: la peinture s'élimine presque en même temps que le vernis.



Fig. 10 Le support en chêne chantourné après la suppression des ajouts en sapin.

chocs ou de chutes: blessures de la couche picturale ainsi que du bois, rupture des joints et formation de cassures verticales. Diverses incrustations en bois de chêne apparaissent (au centre et à gauche du joint gauche dans l'arrondi supérieur de la chaise, dans la grande volute de droite, dans la pomme ainsi qu'à gauche de la charnière inférieure de la porte).

Tout autour du chantourné et à environ 2cm de la rive biseauté, on retrouve des trous de clous. Deux clous subsistent d'ailleurs, une dans la pomme et l'autre dans la grande volute de droite. La transformation du chantourné en tableau rectangulaire a entraîné le rabotage en surface du bois de chêne original à divers endroits pour niveler l'assemblage entre les deux supports. L'application du parquetage a nécessité l'amincissement du support original: à présent il ne mesure plus que 0,4cm. Le parquetage devenu fixe a emprisonné le support original et provoqué la rupture de plusieurs joints et fentes antérieures.

b. Le support en sapin. Le parquetage a contraint le support en sapin. Les planches en sapin, bois plus tendre, se sont déformées en épousant le montants du parquetage. Les joints non recouverts par les montants verticaux ont éclaté. L'assemblage entre le support en chêne et celui en sapin s'est partiellement disjoint.

La couche de préparation

Technique picturale

a. Le support en chêne. La préparation à base de blanc de plomb est très mince et de couleur brun clair. Les rayons X (Voir fig 3,4) montrent que cette préparation a été appliquée à l'aide de larges coups de brosses horizontaux. Les I.R. n'ont révélé aucune trace de dessin.

b. Le support en sapin. Il est recouvert d'une fine couche de préparation à base de craie et d'huile de lin.

Etat de conservation

a. Le support en chêne. La préparation adhère bien au support et est en bon état de conservation. Elle est absente dans diverses lacunes accidentelles affectant le panneau. Elle a par contre été délibérément éliminée par le rabotage du support lors de la transformation du chantourné en tableau rectangulaire afin de niveler les différents joints.

b. Le support en sapin. La préparation se soulève le long des joints.

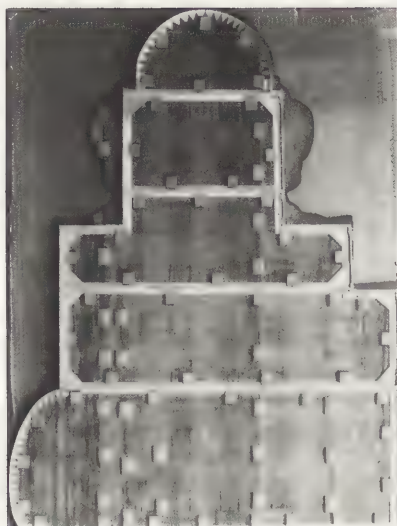


Fig. 11 Le revers du chantourné a été consolidé par une armature en aluminium.

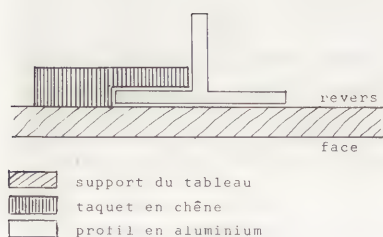


Fig. 12 Coupe transversale de l'armature en aluminium, posé au revers du support.



Fig. 13 Détail de l'armature en aluminium.

La couche picturale

Technique picturale

a. *Le support en chêne.* La matière picturale à liant huileux est fine, très fluide et dure. Elle adhère bien à la préparation et épouse les fibres ligneuses du chêne. Elle est appliquée en couches successives qui sont, tantôt couvrantes, tantôt transparentes. La palette est vive et harmonieuse. Par endroits, les coups de pinceaux sont larges et fondus, en d'autres endroits, ils sont nets et déliés. Ça et là, de légers empâtements suggèrent le volume ou accrochent la lumière. Les craquelures sont très fines et presque inexistantes en raison de la finesse de la couche picturales. Elles sont plus apparentes dans les empâtements à base de blanc de plomb.

La signature JOHA SPRONCK AN 1654, peinte à droite sur le rebord de la tablette, est fortement usée et a été partiellement surpeinte lors de la restauration de la fin du XIX^e siècle: zones mates par-dessus le vernis.

b. *Le support en sapin.* La peinture à l'huile brune du fond est fine et atténue fortement l'effet de trompe-l'oeil. La facture picturale est médiocre: de larges coups de pinceaux sont brossés verticalement et en oblique, servant essentiellement à recouvrir le fond plutôt qu'à faire ressortir le sujet principal. Elle contraste avec la finesse des touches et la vivacité des couleurs de l'enfant endormi.

Etat de conservation

a. *Le support en chêne.* La couche picturale a souffert des nombreux nettoyages domestiques et des interventions antérieures. Des glacis ont été éliminés, surtout dans les carnations et les zones d'ombres. La matière picturale est usée sur la crête des fibres ligneuses. D'importants masticages et surpeints ont été appliqués pour dissimuler les divers joints, incrustations et assemblages.

b. *Le support en sapin.* La peinture présente plusieurs soulèvements le long des deux joints de droite.

Le vernis

Une épaisse couche de vernis brunâtre recouvre toute la surface picturale. Un rectangle mat, résultant d'une application d'un solvant trop puissant par un expert restaurateur de passage, s'observe sur le rebord de la tablette de la chaise. L'examen aux U.V. dévoile les nombreux surpeints ainsi qu'une accumulation de vernis tout autour de la signature et la date.

La restauration

La première étape de la restauration a consisté dans l'allègement progressif de l'épaisse couche de vernis avec un mélange d'isooctane-isopropanol. Quelques rectangles ont été éclaircis: des couleurs chatoyantes sont apparues. Par contre, la peinture brune du fond se dissolvait presque en même temps que le vernis. Les nombreux surpeints, retouches et masticages, qui en divers endroits débordaient sur la couche originale, ainsi que les restes de colles désagrégées, subsistant dans les joints et fissures, ont pour la plupart été éliminés au scalpel (Voir fig.8,9). La région de la signature et de la date n'a été que partiellement dévernée afin d'éviter toute pénétration de solvant et risque d'usure.

Le dévernissage terminé, on découvre l'aspect original de l'oeuvre: un trompe l'oeil chantourné. L'état peu satisfaisant du support en sapin, la dénivellation le long du contour du chantourné, les fissures et certains joints ouverts d'une part, le contraste entre le fond brun grossièrement brossé et la facture picturale minutieuse et la palette très colorée avec de subtils effets d'ombre et de lumière d'autre part, nous ont amené, en accord avec le propriétaire, à dégager l'oeuvre originale en la libérant de son parquetage et des ajouts en sapin³ (Voir fig.10).

Le revers dégagé du support en chêne a été soigneusement nettoyé de toute trace de colle. Les creux dans le bois ont été rebouchés avec un mélange de sciure de bois de chêne ancien et d'acétate de polyvinyle en émulsion. Les joints et fissures



Fig. 14 J. VERSPRONCK. *Enfant endormi*. Le trompe l'oeil chantourné après la restauration.



Fig. 15 Détail de l'enfant après la restauration.

ont été réajustés dans la mesure du possible et recollés avec ce même adhésif. Ils ont été renforcés par une série de petits taquets en vieux chêne. Pour consolider ce "chantourné", fortement aminci lors du parquetage, et pour éviter toute surcharge à ce support de 0,4 cm d'épaisseur, nous avons opté pour une armature légère en aluminium (Voir fig. 11,13). Cette armature repose contre le tableau sans y être fixée, en couissant dans des petits taquets profilés à mi-bois et collés en surépaisseur sur le revers du tableau (Voir fig.12). Un profil en L épouse les contours du chantourné: il est échancré et cintré dans la partie haute de la chaise ainsi que dans le dos du chat; il est rectiligne dans les parties droites. Quatre traverses horizontales profilées en T rejoignent les montants verticaux. Ces profils sont assemblés entre eux à l'aide de petites languettes, courbées ou pliées à angle droit selon leur emplacement et fixées à l'aide de rivets. Certains coins sont consolidés par des triangles, rivetés au montant en aluminium.

Le traitement du revers terminé, celui de la face picturale a été continué. Les différents joints, fissures et lacunes ont été mis à niveau avec un mastic à base de kaolin et colle animale sans pour autant masquer tous les dégâts subis au cours des temps. Ils ont été imprégnés à la cire et colorés à la détrempe maigre dans une ton brun. Le tableau a été vernis à la brosse avec un vernis à retoucher Talens. Les retouches finales ont été réalisées avec des pigments secs mélangés au vernis à retoucher. L'oeuvre terminée a été recouverte par un vernis final Talens, appliqué au pistolet (Voir fig. 14, 15).

L'artiste Johannes Verspronck 1597-1662

Johannes Verspronck naquit, vécut et travailla à Haarlem de 1597 à 1662⁴. Il peignit essentiellement des portraits grandeur nature de personne appartenant à la bourgeoisie de Haarlem. Les hommes sont tournés de trois quart vers la droite, les femmes de trois quarts vers la gauche. Ils sont pour la plupart représentés assis ou debout, à mi-corps, parfois en buste ou jusqu'aux genoux, exceptionnellement en pied. Verspronck peignit également quelques "portraits de groupe" représentant des Régents ou Régentes d'un hôpital, orphelinat ou autre institution religieuse.

Les premières oeuvres connues datent de 1634 et reflètent l'influence de F. Hals, surtout au niveau de la composition. Sa technique picturale par contre est moins nerveuse et spontanée, mais plutôt précise et délicate, avec un grand souci du détail et des accents de lumière.

Ses nombreux portraits d'adultes sont peints avec réalisme et sobriété, conformément à la rigueur austère de la Hollande du XVII^e siècle. Par contre, les rares Portraits d'enfants sont exécutés avec plus de liberté, de charme et de naturel. Tout à fait remarquable est le tableau représentant "Les Régentes de la maison de Saint-Esprit" datant de 1642 et conservé au Frans Halsmuseum de Haarlem. Quatre régentes plutôt austères sont interrompues en pleine réunion par deux orphelins et une surveillante leur annonçant, avec un sourire malicieux, que l'un d'eux a fait un accroc dans sa manche. Si les visages des autres dames sont graves et sérieux, ceux des enfants sont charmants et pleins de naturel. Ce réalisme rejoint celui de l'enfant assoupi dans sa chaise haute.

La signature de JOHA SPRONCK AN 1654 ressemble fort à celles rencontrées sur les nombreux portraits peints par Verspronck.

Le trompe l'oeil chantourné = dummy board figure

Les personnages découpés et peints grandeur nature en trompe-l'oeil pour donner l'illusion d'une présence humaine sont appelés selon un terme anglais *Dummy board figure*. Ils étaient placés à une certaine distance du mur afin de créer une ombre et renforcer l'effet de trompe-l'oeil. Pour les réaliser, l'artiste dessinait les contours du personnage sur un support rectangulaire. Le bois était ensuite minutieusement découpé suivant les contours exacts de la silhouette. Les rebords étaient biseautés vers l'arrière afin de ne pas laisser voir l'épaisseur de la planche.

L'idée d'un tel découpage est probablement liée aux recherches effectuées dans la peinture décorative et de trompe-l'oeil, très en vogue dans la peinture murale

italienne du XVI^e siècle. Elle peut également s'être inspirée des figurants peints utilisés dans le théâtre italien⁵.

On ignore encore où elles ont été peintes pour la première fois. Toutefois, on rencontre fréquemment des gentilshommes, des élégantes, des domestiques, des enfants et des soldats en Hollande, en Angleterre, en Allemagne et en Autriche. Ont-ils été ramenés par des artistes des Pays-Bas, ayant séjourné en Italie, vers 1630 ? Houbraken écrit en 1719⁶ que C. Bisschop (Dordrecht 1630–1676) était le premier "à imaginer et à peindre des figures avec des couleurs vives sur panneaux et d'en découper les contours". Elles étaient placées dans un coin de la salle de séjour ou au fond d'un vestibule pour y figurer comme "personne vivante". Ces silhouettes étaient imaginées avec beaucoup d'ingéniosité, de naturel et de précision. Certains personnages étaient peints en clair-obscur et tenaient un bougeoir à la main. Une bougie était allumée à la tombée du jour.

Jusqu'à ce jour, plusieurs historiens d'art se sont penchés sur les "Dummy board figure" mais ils ne disposaient d'aucun exemple signé ou daté⁷.

Conclusion

Cette restauration a permis à un tableau, défiguré pour des raisons commerciales, de retrouver sa destination originale telle que l'artiste et son commanditaire l'ont désiré: celui d'un objet décoratif servant à créer une présence humaine dans la pièce de séjour. C'est le seul témoin signé et daté d'un trompe-l'oeil chantourné hollandais du XVII^e siècle connu à ce jour.

Ce cas pose un problème fondamental au restaurateur face aux nombreux tableaux transformés et défigurés par des interventions antérieures: faut-il oui ou non retourner à l'aspect original de l'oeuvre?

Notes

- 1 L'examen aux R.X. et I.R. a été réalisé au Laboratoire d'étude des oeuvres d'art par les méthodes scientifiques dirigé par le Professeur R. Van Schoute (UCL).
- 2 D'une part, on observe du bois de chêne, recouvert par le blanc de plomb de la préparation, qui s'est incrusté dans les fibres ligneuses. D'autre part on voit une zone plus foncée sans traces de préparation avec deux grand noeuds, assez typiques du sapin.
- 3 Ce travail minutieux a été réalisé par Jozef Grosemans, ancien restaurateur de panneaux à l'Institut Royal du Patrimoine Artistique de Bruxelles. Il élimina le parquetage et les éléments de sapin; il confectionna l'armature en aluminium.
- 4 R.E.O. EKKART, Johannes Corneliszoon Verspronck. Leven en werken van een Haarlems portretschilder uit de 17-de eeuw, Zaandam, Drukkerij C. Huig b, 1979.
- 5 A.C. SCOTT, Dummy board figures, Cambridge, The Goldon Head Press, 1966; J. DE KLEYN, Dekoratieve figuren in huis, Antiek, 1966–1967, p. 31–36; C. GRAHAM, Dummy board and chimney boards, Aylesbury, 1988, Shire album n°214.
- 6 Arnold HOUBRAKEN (Dordrecht 1660–Amsterdam 1719) était peintre, graveur et historien d'art. Il a écrit *De Groote Schouburgh der Nederlantsche Konstschilders en schilderessen*, vol. II, Amsterdam, 1719. Nous faisons référence à l'édition P.T.A. Swillens, Maastricht, 1944, p. 173.
- 7 Je profite de l'occasion pour remercier le Professeur R.E.O. EKKART, directeur du Rijksbureau voor Kunst-historische Dokumentatie à la Haye, qui, s'intéressant aux "dummy board figure" me confirma cette information.

Abstract

The conservation of a panel painting whose wood and polychromy were heavily damaged, from the first decade of the 16th century, gave us the opportunity to plan, develop and apply a new device for the conservation and proper maintenance of wooden panel paintings.

The five boards of the main picture have been joined with a support structure which followed the movements and displacements of the whole and of each single board in three directions.

The planning of the support structure was based on positive experimental tests, non-destructive methods and aesthetic criteria for minimum visual disturbance. After this first experience we began to produce other mechanisms of our own invention, which were greatly improved both aesthetically and functionally by the use of a clasp plug with ball knuckle joint and flexible sleeve (*patent pending).

Keywords

Wooden panel painting, support structure, mobile clasp mechanism, aesthetics, durability

Practical Solutions to Preserve Panel Paintings: Preliminary Report on Structural Mechanisms

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Introduction

This report describes our efforts to devise new methods for the structural support of panel paintings. It will not detail the evolution of cradling systems over time nor the damage that some of them have caused to wood and polychrome surfaces; further information on these topics may be found in the references cited in the accompanying bibliography.

At the base of our project is the idea of "minimum intervention", i.e. the effort to maintain the integrity of the work of art by preserving as much as possible its historical traces. Each work of art has its own identity: because of its aesthetic characteristics, the way in which it reveals itself to the spectator, and its conservation requirements, it is the work itself that prompts the conservator to determine the best conservation approach. The conservator must recognise these requirements and take them into consideration when elaborating new ideas and applying suitable methods.

The altar-piece of St. George: history and conservation

The 14th century church dedicated to St. George in Carpaccio (Friuli Region of Italy) houses a retable with a panel painting signed and dated 1508. The altar-piece was originally made of two different pictures, which were badly assembled in the 18th century inside a 17th-century wooden altar which had also been heavily transformed. The main panel, made of five boards of poplar 200 cm high and 19, 40, 26, 42 and 28 cm wide, represents the Virgin with the Child and the Saints Sebastian and George; in the upper triangular panel, there is Christ resurrected with two angels.

Over time the original polychromy was covered with six layers of overpaint and the wooden panel was heavily affected by wood-worms, the settling of the original transverse bars and very bad maintenance, an example of which is the nailing of the perimeter to the altar frame. These caused the complete detachment and independent warping and curving of the boards, cleavage, buckling and collapse of the ground/paint layers.

Based on the scientific and historical data collected, on the real needs as prompted by the panel itself, and the directives of the Italian Soprintendenza, we set up our philological work as follows:

- conservation and aesthetic restoration of the constitutive materials of the work of art (wood, ground and polychromy);
- recovery of the original shape and dimensions of the two pictures (rectangular painting and triangular tympanum) which ruled out their replacement inside the wooden altar;
- planning and construction of a new containing structure i.e. an altar;
- the resolution of conservation problems through research into an adequate microclimate and a support structure, i.e. cradling.

The conservation and aesthetic work were extensive; here we shall simply point out that the whole has been reassembled by gluing the five boards along their edges with a reinforcement of hard wooden pins, as in the original, without using any *sverzatura*. Analysing the data, we came to the following conclusions:

- the original polychrome surface is much wider than the span of the ancient altar; its replacement in the altar would have interfered with the reading of the composition in its graphic and formal completeness;



Fig. 1—Back of the panel painting of St. George inside the open microclimatic frame box.

- the panel painting goes back to the first decade of the 16th century, whereas the altar is 18th century, subsequently modified;
- the altar has a curved span, whereas the panel has rectangular and triangular shapes.

We began to plan a new frame basing our research on historical, artistic, typological, graphic and iconographic methods; the result was a new altar with a tympanum connecting the two panels in a essential shape. Its inside has a microclimatic environment with controlled RH to reduce the movement of the panels to a minimum (See fig. 1).

Continuing our research into the ideal maintenance of the work of art, we did not probe into the fundamental problem of microclimate—which we tried to solve in part with the new frame box—but we analysed the problem of cradling, that is the application of a support structure to this particular work, and the new applications arising from it.

Support structure

In order to provide a level support to the painting, a structure commonly described as a cradle or “parchettatura” was indispensable. In our report we shall not use these words, which refer to a mechanism widely different in method, foundation and purpose. Our solutions will be called and better defined as “support structures”.

Very good methods of joining the boards of a panel, which took into account the real requirements of the panel itself, were suggested many years ago in various papers such as the studies by Roberto Carità, which suggested the adoption of a truly sliding transverse bar (1,3); but in reality few conservators followed those directions. Only in recent times can we find a renewed interest and a mature sensitivity flowing into good technical and operative results, and all agree that mobility between panel and support structure is indispensable.

Our plan for a support for the paintings of St. George and also our other proposals are founded on the following important considerations:

- 1—Mobility. The support structure has to allow wood the possibility of following its natural movements, often caused by the impossibility of maintaining an adequate microclimatic control. Such mobility prevents the concentration of extreme forces inside the original panel, forces that may cause heavy damage to wood and polychromy.
- 2—Support. As well as favouring the maximum freedom of movement, the structure must provide adequate support to the wood. It could be compared to an octopus, whose tentacles yield to arising stresses, but which keeps the boards together at the same time.
- 3—Easy to construct. To conservators, an important point is to have a support structure that is simple to produce and easy to apply.
- 4—Non destructive. Many practices in the past involved planing down panels with partial or total thinning of the original wood. Our proposal advocates minimum intervention, possibly avoiding the flattening of surfaces to facilitate the sliding of transverse bars and the insertion of cleats. Furthermore we wanted a mechanism which did not necessarily involve warp flattening.
- 5—Good aesthetics. We thought it was important, in order to respect the originality of the work of art, to maintain an attractive appearance on the back as well, keeping it free of complicated and bulky mechanisms.
- 6—Philological honesty. The back of a panel painting is as important as the front, because the traces of its historic vicissitudes carry fundamental information on its author, his technique, his environment and so forth. We were also favourably impressed and inspired by the back of a panel from the 13th–14th century, warped but still in good condition, which was supported by simple wooden bars perpendicular to the panel.
- 7—Use of durable materials. A support structure has to be made with materials

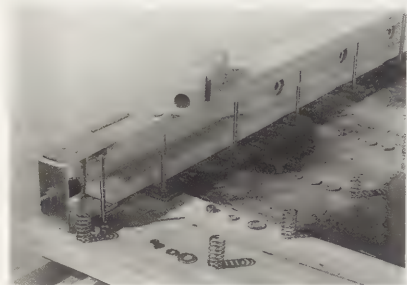


Fig. 2—Transverse bar of the support structure for the painting of St. George during assembly.

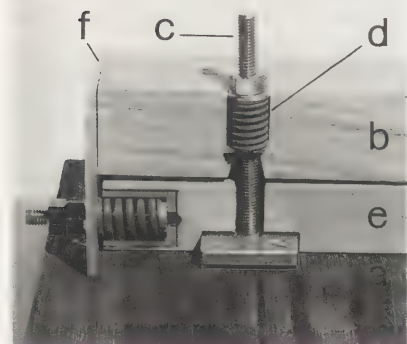


Fig. 3—Head of transverse bar with mechanism for lateral push. a: original panel; b: "U"-shaped wooden transverse bar; c: brass plates with wooden veneer and threaded bar; d: aluminium sleeve, spring, washer and nut; e: lateral push mechanism with sliding wooden core, aluminium sleeve, spring, threaded bar, nut; f: "U"-shaped aluminium profile.

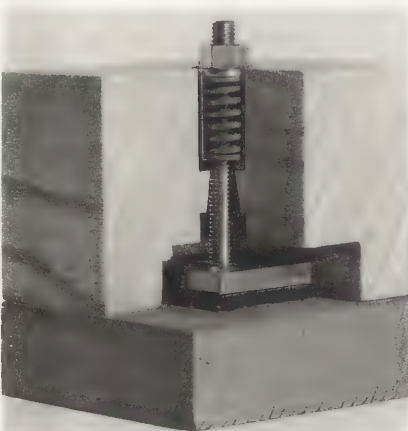


Fig. 4—Clasping mechanism: detail of plate on rubber buffer surface.

that guarantee safety and allow for easy maintenance in the future, with consequent advantage for the wooden panel and polychrome surfaces.

To work properly, a support structure must find an equilibrium with the boards of the panel. However this should be a one-way, not a mutual relationship: in fact it is the support structure that has to recognise and yield to all in-plane and orthogonal movements that the panel develops, and bring them onto itself. If in this analysis we neglect the stresses imposed by a traditional cradling, as a result of its constitutive material, i.e. wood, we can notice that damage to the work of art is caused above all by the inability of the cradling to yield to in-plane (swelling and shrinking) and perpendicular (warping) movements of the boards.

Taking the foregoing evaluations, projects and experiments on prototypes into proper consideration, we devised a mechanism—then applied it to the painting of St. George—which made use of classical wooden transverse bars connected to the panel by springs perpendicular to the longitudinal axis of the bar, and endowed with a lateral sliding force, also provided by springs, parallel to the longitudinal axis of the same bar. We built four "U"-shaped transverse bars in ash (See figs. 2,3), and a series of brass plates (25×25 mm) in the centre of which a threaded bar was fixed and on whose lower side a wooden veneer was glued as a buffer surface for thermic bridges and possible removals.

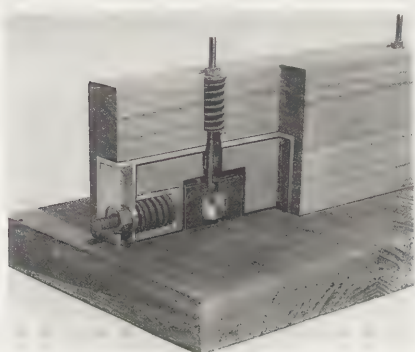
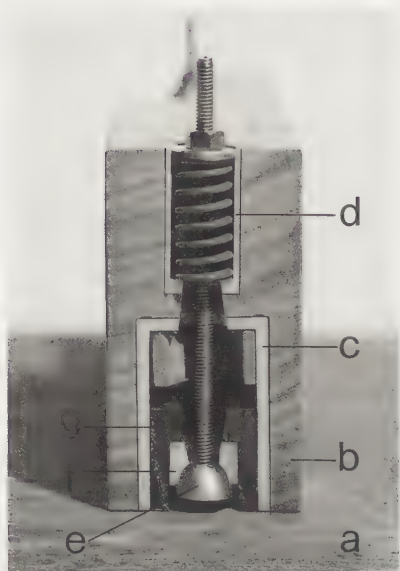
The plates were glued to the back of the panel, reinforcing the adhesion with two short brass screws because of the weakened worm-eaten wood; we thought that it was better to use short screws rather than fix plates mounted onto new wood connections or into recesses carved in the original wooden support. Then we produced, inside the transverse bars and in connection with the plates, passing-by holes to lodge aluminium sleeves—a material which favoured lower friction forces and higher precision—and their inner springs. The springs would give the necessary traction force and follow the warping of the panel as well, the latter hopefully reduced also by the microclimatic box frame. Having coated the transverse bars with paraffin and located them in the exact position, we did obtain a rather functional support structure: the mobility of the structure in favour of free warping is ensured by springs, while longitudinal sliding is ensured by the flexibility of the "threaded bar-spring" system, the increased dimensions of the sleeve with respect to the size of the spring itself, and the conical shape of passing-by holes.

Further improvement was obtained by supplying a lateral push through a piston-and-spring mechanism mounted at the two ends of the transverse bar, adequately reinforced by an aluminium "U"-shaped profile, and put on the first external plates. Here too, the spring is lodged in an aluminium sleeve which allows the best running and a good regulation of forces through the nut that blocks the pushing piston (See fig. 3).

The validity of this mechanism lies in its simple execution, thanks to the material employed, i.e. wood; in good aesthetics, because the whole mechanism is lodged inside transverse bars; in good mobility and low friction, further reduced to a lateral sliding force. This allows the boards to stick together and to overcome the friction detachment force caused by possible movements.

The above-mentioned system was applied to the painting of St. George five years ago. Today the panel is still in very good condition, without any separation of the joints of the boards.

After this operating experience we wished to continue our research, so we created a few more prototypes. The possible modifications concerned transverse bars and bonds between the support structure and the original panel. We must remember that the great strength of the bars (50×55 mm) depended on the need to place the mechanism inside a housing structure made entirely of wood, but this could be lightened and dimensionally reduced by using other materials i.e. aluminium, by reducing the contact surfaces between transverse bars and panel and the distance between springs and plates. The very strong bond could be eased by inserting a buffer surface in elastic material, i.e. rubber, between panel and plate (See fig. 4); but in so doing, the critical point of traction forces



Figs. 5, 6—Clasping plug with ball knuckle joint. a: panel; b: aluminium transverse bar; d: aluminium core; e: aluminium sleeve, spring, washer and nut; e: brass half-sphere with threaded bar; f: concave Teflon cap; g: hard wood plug. The mechanism for lateral push is similar to the one in Fig. 3.

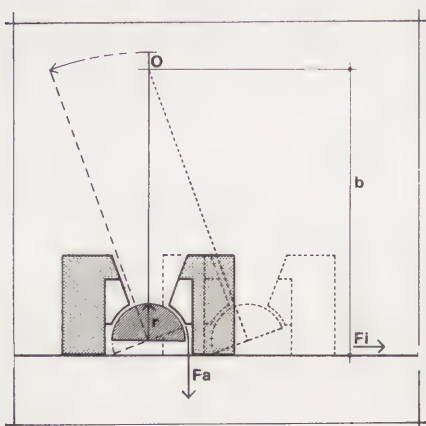


Fig. 7—Graphic of displacements.

applied to the springs would act more on the adhesion force of the three materials (wood, rubber, brass), and because of the difference of materials and the absence of fixing screws, we thought that this mechanism was more suitable for light and small panels where high traction forces do not usually develop.

So we devised a new system where plates, although fixed to the panel, could offer the threaded bar a higher mobility in all directions. We preferred not to use "slide" solutions—that is, an element in Teflon or nylon running inside a metal channel fixed to the panel—but instead chose a clasping plug with a spherical knuckle joint, i.e. a plug in hard wood, inside which there is a passing-by slot. There a brass half-sphere with a steel thread bar is lodged in a Teflon cap. The wooden plug is glued to the panel, and the bar linked with the half-sphere can move in all directions, developing a very low friction force (See figs. 5,6).

Unlike the "slide" mechanism, ours does not give rise to flexing movement; furthermore, the bond, i.e. the mutual position of half-sphere and cap, does not change during displacement.

Panel-induced forces (equivalent to F_i) generate the displacement of plugs and consequently the rotation of half-spheres. The centre of rotation clasps the centre of the half-sphere's base. During its movement the whole mechanism does not change its shape, but maintains the same distribution of forces, which occurs only with difficulty in a "slide" mechanism. The effort required to displace the plug is lower than the one developing in the above-mentioned mechanism. This can be argued by the equilibrium conditions of our mechanism, proved by the equality of the two movements:

$$F_i b = F_a r$$

where b is the arm, i.e. the distance between the contact point of the panel and plugs and the upper edge of the sleeve hanging the spring (shrinking or swelling) with fulcrum in O, and F_a is the summation of friction forces (See fig. 7).

On the contrary in a simple "slide" mechanism the expansion force F_i is equivalent to the resistance force F_a . As is evident in our case the ratio between b and r will always be higher than 1 and consequently our F_i will always be much lower than F_a , in other words, a much lower force is sufficient to oppose F_a itself.

This mechanism is dimensionally close: the plug is $30 \times 20 \times 20$ mm, the diameter of the half-sphere is 13 mm and that of the Teflon cap is 15 mm, with further reductions as necessary. In this kind of mechanism, screws between plugs and wooden panel are not used and the use of glue is preferred; this will create a sort of safety valve if very strong stresses arise during high climatic variations; in fact plugs themselves would easily detach in this case with no damage to the panel painting.

Another prototype supplied with the above-mentioned device is a "U"-shaped transverse bar in hard wood in which an aluminium profile is inserted; in the upper part there is the housing for the sleeves, and here too the piston for the lateral push is in wood and clasping plugs are as described above (See figs. 5,6).

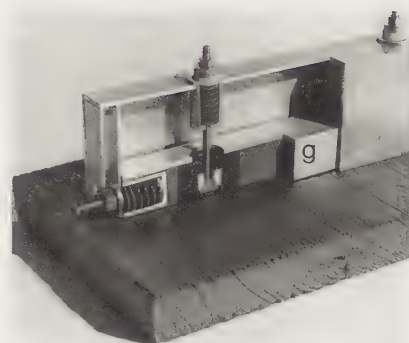
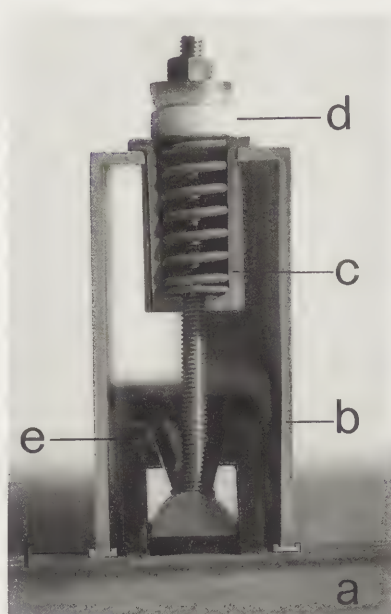
The technical advantages of this model are lightness and reduced overall dimensions. Here the mobility of the transverse bar is high and with low effort: displacement can reach 16 mm and over (See fig. 8).

We could verify that the pressure exerted by the round washer on the upper side of the springs is not quite even because of its sloping during movement. Furthermore plugs could not have too much play inside the "U"-shaped profile in the longitudinal direction of the fibers; this displacement is of no importance in normal conditions but it would be dangerous in the presence of irregularities in the wooden fibers (knots, waving and so forth).

Thinking of a possible solution to these problems we designed another mechanism, all in aluminium for maximum versatility (See figs. 9,10). It differs from the above-mentioned one by the presence of slots in the upper side of transverse bars, into which aluminium sleeves are inserted with clicks blocking them when



Fig. 8—Extent of displacements of the mechanism in Figs. 5, 6.



Figs. 9, 10—Clasping plug with aluminium transverse bar. a: panel; b: aluminium transverse bar; c: aluminium sleeve and spring; d: concave Teflon neck with brass half-sphere and nut; e: clasp plug with ball knuckle joint; f: Teflon layer; g: aluminium piston for lateral push.

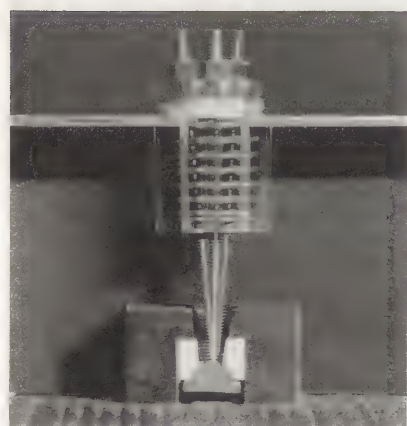


Fig. 11—Extent of displacements of the mechanism in Figs. 9, 10.

the spring goes in tension. The round washer is replaced by a Teflon concave neck clasped to the spring; in the upper part the system is blocked by a brass half-sphere and a nut. Here the piston for the lateral push is in aluminium and the clasping plugs are narrower than the inner span of the transverse bars.

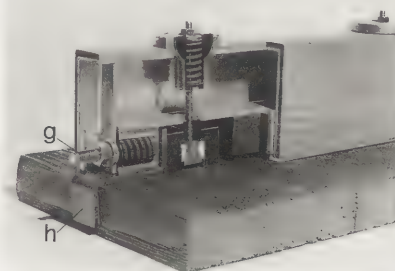
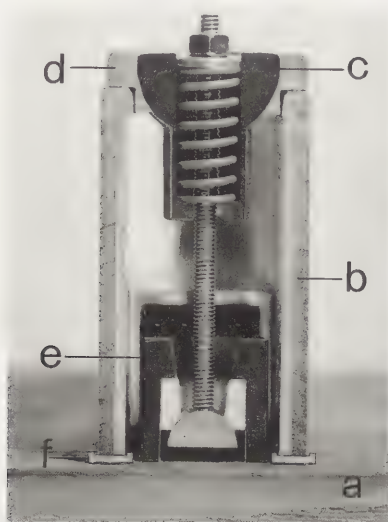
The advantages of this model are good aesthetics, lightness, functionality and extreme practicality of mounting and operation. The only arguable point is its mobility, which is a bit lower because of the shorter diameter of the hole in the upper part of the Teflon neck (See fig. 11).

Some performance of the mechanisms described so far could be further improved, that is: lateral push and amount of displacement in all directions.

Formerly the entire lateral push was loaded on the first two or on the first two couples of plugs at the ends of the transverse bars; a definite advantage would come from lowering the point of application of forces by bringing it near the axis of the panel's thickness for a better distribution. Furthermore, good displacement also depended on the length of the threaded bar and consequently on the thickness of the transverse bars.

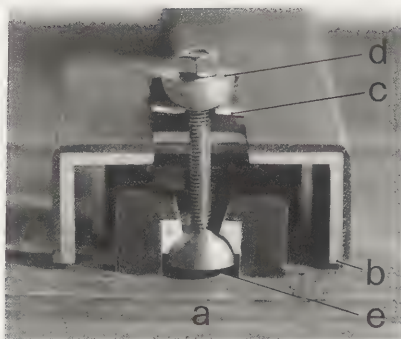
The improved system consisted of a "U"-shaped aluminium profile covered with a thin veneer of wood (2 mm) (See fig. 12), so we could combine the functionality of aluminium with the aesthetics of wood.

A lower application point of forces was obtained with a "Z"-shaped steel element (See fig. 13): one end leans on the side of the panel, the other one is inserted



Figs. 12, 13—Clasping plug with flexible half-sphere. a: panel; b: aluminium-wood transverse bar; c: brass half-sphere and spring; d: brass or Teflon cap; e: clasp plug with ball knuckle joint; f: Teflon foil; g: aluminium piston for lateral push; h: "Z"-shaped steel element.

between piston and plug. So the force can be distributed either on the first and second plug or on the side of the panel; this means that for large panel paintings, requiring stronger support structures, an excessive shearing stress cannot injure the juncture between panel and plugs. Displacement capability was improved with a flexible sleeve and spring. The new brass sleeve has a spherical upper edge based on a brass or Teflon cap; this one by means of a click, is inserted into a proper housing in the upper side of the transverse bar. With the model endowed with such a device we could obtain displacements of some centimetres, and at the same time maintain the traction force parallel to the axis of the spring (See fig. 14). These technical devices are allowed a further reduction of the height of the transverse bar without any damage to the functionality of the system.



Figs. 15, 16—Clasping plug with semi-elliptical spring. a: panel; b: aluminium-wood transverse bar; c: semi-elliptical spring; d: brass half-sphere and nut; e: clasping plug with ball knuckle joint.

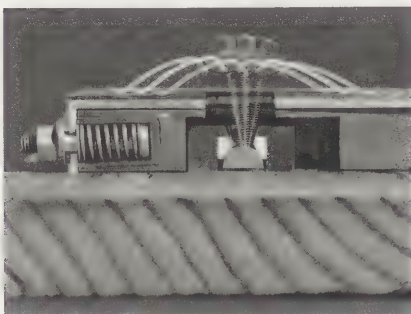


Fig. 17—Extent of displacements of the mechanism in Figs. 15, 16.

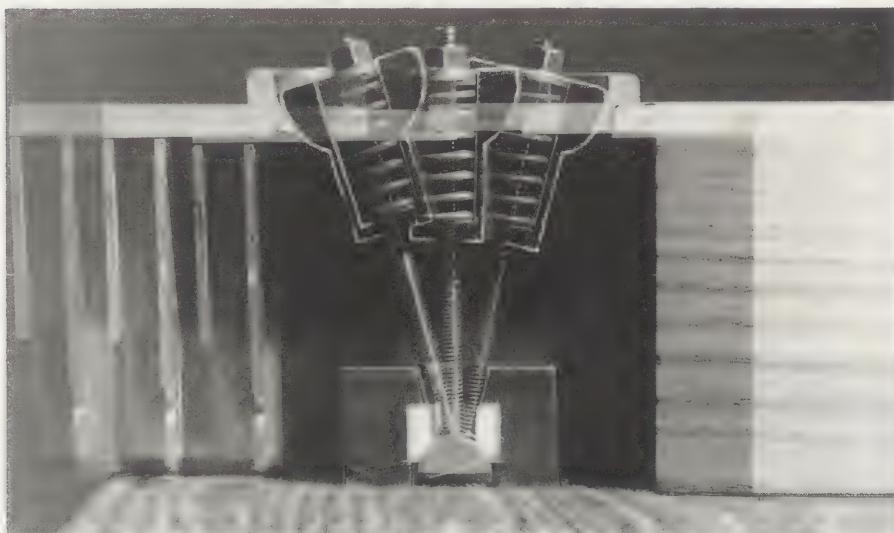


Fig. 14—Extent of displacements of the mechanism in Figs. 12, 13.

All mechanisms described so far are suitable, because of their constitutive pattern, above all for large panel paintings; for the small ones we devised a different mechanism whose dimensions and weight could be reduced to a minimum.

So we built a "U"-shaped aluminium profile, covered with a wooden veneer, 15 mm wide (See figs. 15,16). The mechanism is a dimensional reduction of the above-mentioned ones, and differs by the substitution of the sleeve and spring with a semi-elliptical steel spring, shaped in the middle to house the clasping half-sphere. The semi-elliptical spring has a central hole to let the threaded bar turn, and raised edges so as not to get stuck in the transverse bar. It has a series of rectangular-shaped holes to let the clasping bar go out with the maximum freedom of movement (See fig. 17); furthermore it allows for the lowering of springs.

Conclusion

The research applied to the conservation of the panel painting of St. George brought us to design and produce other types of support structures. We wish to point out that they are subject to possible modification according to the evaluation of each individual work and surely they can be taken as a stimulus to continue with the research undertaken to date. Our ideas were intended to conform to a series of principles, as stated above, and we verified that all our operative techniques could satisfy them thoroughly. A point of particular interest concerns the transverse bars, the placement of which no longer requires the flattening of warped panels: transverse bars of whatever material they are made—wood, aluminium, aluminium plus wood—can be shaped as required and follow the shape and warping of the panel.

For a further lowering of friction force between panel and transverse bars it is possible to insert a thin layer of Teflon or PVC or other material which favours more independent movement between the panel and the support structure.

Another recommendation is to round the edges of the transverse bars so that they slide better, and to coat the whole mechanism with silicon spray even though it is rustproof.

We can conclude that this research put forward three operative solutions:

1—Clasping plugs with ball joint. Our mechanisms come with square or rectangular wooden elements; however it is also possible to make round ones. This modification can be used in case it is necessary to insert the plugs some millimetres into the original panel because of bad conservation of the original wood.

2—Lateral push. This force allows lowering of friction force and joining the boards together by pushing them towards each other to avoid cracks caused by positive inner friction forces. The piston can be supplied with a "Z"-shaped steel element which lowers the application point of forces and offers a better distribution of push.

3—Mobility. It is further improved by the clasping plug with a sleeve in a semi-spherical cap always capable of maintaining the force of the springs in the right position, even during the displacements of clasping plugs.

Our aim was to devise a real mobile support structure; we hope that our proposal will be a contribution to the research to save the artistic heritage of panel paintings.

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Abstract

Pauline Augustin combined several materials to obtain a larger support than was normally used for an ivory portrait miniature painted with watercolours. To obtain the 212 × 116 mm large support, thin ivory plates were assembled along opposite grain directions and glued to cardboard with shellac. The shrinking of the ivory caused severe cracking of the miniature. Later restoration measures, such as overpainting and scraping the paint layer, worsened its condition. The treatment of the support focused on the conservation of the original combination of materials, is described as well as the paint layer restoration.

Keywords

Miniature, portrait, watercolour, painting support, ivory, grain direction, cardboard, shellac, cracks



Figure 1. Portrait of a general by Pauline Augustin, 1822, watercolour on ivory, 212 × 166 mm, prior to restoration.

A Large Ivory Miniature: Conservation Problems of the Support

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Introduction

The restoration of the portrait of a general painted by Pauline Augustin in 1822 (See fig. 1) required a detailed study of the assembled support. The portrait has unusually large dimensions (212 × 166 mm) for a representation painted in miniature technique on ivory. In general, ivory sheets are cut in the direction of the longitudinal grain, and their width is limited by the diameter of the elephant tusk. To realise a larger support, the artist combined several materials. Unfortunately, this construction was not a very stable one.

The use of ivory as support for water colours

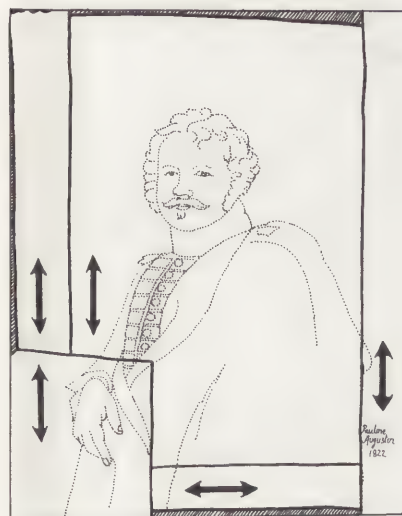
Since the beginning of the 18th century, artists discovered the ideal quality of a smoothly-planed ivory plate for miniature painting. The use of water colours in a stippling manner gives the portrait a very vivid appearance on the slightly transparent ivory. As the use of this painting technique rapidly expanded, the technique was perfected. In the early 19th century, the artists were asked to produce larger miniature portraits. Therefore, some artists used paper or cardboard as a watercolour support. Isabey introduced a paper with a parchment-like appearance stretched over a metal plate (1). Others used ivory cut in veneers around the circumference of the tusk to increase the size of the plates (2). Such miniatures are subject to heavy warping. Jean Anthoine Laurent inlaid ivory sheets for the flesh tones of the face and hands into thick cardboard (3). In this case, the different tensions of the materials caused severe problems.

But what did Pauline Augustin do to realise her "megazine" with a full ivory surface as a painting support? Pauline Augustin (1781–1865) was the best pupil of Jean Baptiste Jacques Augustin, a well-known French miniaturist of the late 18th and early 19th centuries (4). Both are noted for their perfect painting technique, including the stippling and hatching of the faces. Certainly, Pauline Augustin tried her best by combining the different materials when she made her paint support. The construction can be compared to the largest paintings by Rubens, who was probably aware of the problems which could arise from assembling wooden boards in different grain directions (5).

The support construction

Four ivory sheets are assembled together in the vertical grain direction and one in the horizontal direction (See fig. 2). Probably Pauline Augustin knew of the possible cracking of the ivory; therefore, she assembled them in a manner to have a middle part of an ivory sheet for the most delicate parts, the face and the hand. The ivory (0.6–0.8 mm in thickness) is glued on two cardboards (each 3.5 mm thick), a yellowish and a grayish one (See figs. 3, 4). Paper and gold beater's skin are mounted on the reverse. The borders are covered with gold beater's skin tape, which originally attached the lost glass to the miniature; this is the method commonly used as sealed protection against dust (6). The glue between the ivory and cardboard layers is shellac, recognizable by its typical orange fluorescence in UV light. The paper and goldbeater's skin are mounted with protein glue. The unevenness caused by the small missing strips of ivory at the left, top, and bottom borders are filled in with a yellowish gesso.

The background of the portrait and the figure's garments are painted with gouache colours. These paint layers cover the joints and gesso fillers (which may have been invisible in the beginning!). The face and hand are stippled in an extremely detailed manner with transparent water colours.



— joints of the ivory plates
 ↔ grain direction of the ivory
 borders with original gesso fillers

Fig. 2: Construction of the support, illustrating the joints of the ivory plates, the grain direction of the ivory, and the borders with original gesso fillers.



----- small fissures in the ivory
 — cracks in the ivory
 — large cracks in the ivory
 point losses because of scraping
 overpaints

Fig. 5: Damages to the support, including small fissures in the ivory, minor cracks in the ivory, and large cracks in the ivory. Damages due to the previous treatments include paint losses because of scraping and overpainting.

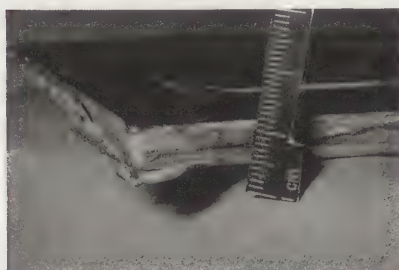
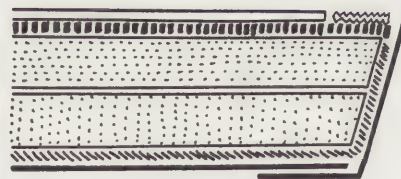


Fig. 3: The construction of the support visible at the lower right corner of the miniature.



ivory
 gesso border
 shellac
 yellow cardboard
 gray cardboard
 paper
 gold beater's skin

Fig. 4: Construction of the support, comprising ivory, gesso border, shellac, yellow and gray cardboard, paper, and gold beater's skin.

Damages and previous restorations

The dimensional variations of ivory, as a function of the changing temperature and relative humidity, vary along the longitudinal, tangential and radial axes (7). Therefore the shrinking of the ivory caused severe cracking of the large middle plate, beginning at the edges of the piece mounted in the opposite grain direction (See fig. 5). As 0.5 mm wide fissures are considered to be much too large for a miniature, they were subjected three times to "restoration." Apparently, prior to the first unpleasant intervention, the borders of the cracks warped, because the ivory lifted up from the cardboard. Instead of trying to reglue the support, the unevenness was scraped, loosening a 1-cm wide strip of the paint layer along the cracks. The whole background and half of the garments were overpainted. A second intervention in a similar manner followed. A third intervention involved filling in the cracks with white gesso and the application of inpainting.

Treatment

How to deal with a support which is constantly moving, was the question of the treatment: should the conservator remove the ivory from the cardboard or reglue the original support?

The second option was chosen. The main reason was to save the original combination of materials; also, the whole support was not warped at all. (Then it would have been extremely difficult to conserve the original gesso borders.) Finally, which new support could be free from new tensions?

The ivory, lifting mainly at the borders and along the cracks, remained fixed to a thin layer of the cardboard. This shows that shellac has enough strength for glueing ivory, which usually is a difficult job (8). This observation, as well as the fact that a newly introduced glue will hardly be reversible behind the ivory, led to the decision to use shellac for reglueing. Each crack was treated separately by the infiltration of ethanol, followed by an infiltration of a low solution of shellac gold lemon in ethanol. In that way, the old shellac was (probably) reactivated. Then, the ivory was pressed down to the cardboard. After drying, the excess of shellac was easy to remove, because the overpainting protected the original paint layer.

The second layer of overpaint, an oil paint, was eliminated with the usual solvents. The first layer of overpaint, a water based one, was tedious to remove. The only way to achieve this was by applying swabs barely dampened in a solution of less than 50% water in ethanol (9).

The cracks were filled with coloured wax as it is a reversible and elastic material, and inpainting was done with solvent-based acrylics.

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Abrégé

L'examen des caisses de retables sculptés devrait permettre de déceler des habitudes locales et des collaborations entre divers artisans. L'exemple décrit est celui de Herbais sous Piétrain (Bruxelles, Musées royaux d'art et d'histoire, inv. 4009). La construction dénote un excellent savoir-faire. Un montant de la huche comporte une marque qui pourrait ici trouver une explication. L'arrière de la caisse est un plancher semblable à certains planchers qu'on a observé comme support des plus anciennes toiles peintes. Il semble que la huche a été polychromée à vide. La polychromie du "remplissage" (groupes sculptés et décor architectural) a été faite en un second temps. Le retable d'Oplinter conservé au même musée (inv. 3196) est construit de la même manière. Tous deux portent la marque d'Anvers, et sont communément datés de vers 1530.

Mots clefs

Retable, menuiserie, marques, polychromie, assemblages, profil, cadres

Retables sculptés et volets peints: Examen de la menuiserie, des profils et de la polychromie des cadres du retable d'Herbais sous Piétrain

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Introduction

L'ancien duché de Brabant a été le siège de la production d'une quantité considérable de retables sculptés, réalisés dans les centres identifiés de Bruxelles, Malines et Anvers [1]. Ces pièces de mobilier religieux sont pour la plupart articulés. Certaines—en assez petit nombre—comportent des volets sculptés; d'autres—c'est la majorité—possèdent ou ont possédé des volets peints.

Les volets ont une fonction de protection et de garde poussière pour les parties dormantes des meubles; ils jouent également l'autre rôle de compléter le déroulement des scènes sculptées accessibles à certains moments bien déterminés de l'année liturgique. Ordinairement l'iconographie des revers des volets—c'est-à-dire des retables fermés—diffère de celle du reste des retables et est consacrée par exemple, à l'Annonciation, à la Messe de saint Grégoire, à des épisodes de la vie d'un saint patron, tandis que l'intérieur des retables est le plus souvent destiné à recevoir des scènes de la vie du Christ (surtout la Passion) et de Marie.

Le lieu d'origine des retables sculptés peut généralement être déterminé par divers critères dont les marques spécifiques de tel ou tel lieu de production. Sauf certains cas isolés, une datation approximative fait l'objet d'un large consensus.

Nous avons appliqué à un retable sculpté à volets peints le même type d'observations que celles que nous avons réalisées sur les panneaux et retables peints [2]. La description du processus de fabrication des retables sculptés vise à déceler des habitudes locales et les liens éventuels entre la fabrication du support des volets peints et ceux de la caisse.



Fig. 1. Le retable d'Herbais sous Piétrain (Bruxelles, Musées royaux d'art et d'histoire, inv. 4009), ensemble.

Le retable d'Herbais sous Piétrain

Nous avons pris comme exemple le retable d'Herbais sous Piétrain. Ce retable est de dimensions modestes (H: ± 178 et L: ± 185 cm) (Voir Fig. 1); il semble qu'à part quelques manques dans l'une et l'autre scène et d'importantes lacunes

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Fig. 2. Le retable d'Oplinter (Bruxelles, Musées royaux d'art et d'histoire, inv. 3196), la caisse.

dans la couche picturale de l'extérieur des volets, le retable n'ait pas subi de transformations et se présente dans son aspect original. La base du retable comporte toutefois une disposition de la polychromie qui trahit l'existence d'une pièce de menuiserie [3] aujourd'hui disparue. La marque d'Anvers (le château et les deux mains) est apposée sur le côté gauche de la caisse. Plusieurs groupes sculptés comportent également des marques en forme de mains. On date ce retable de 1530, comme d'ailleurs le retable d'Oplinter qui porte également les marques d'Anvers.

La caisse

Pour comprendre les étapes de la construction de la caisse, nous nous sommes aidés-outre de l'observation directe-de photographies réalisées lors de la restauration des retables d'Herbais et d'Oplinter (Fig.2). Nous proposons une reconstitution des étapes de la construction du retable d'Herbais (Voir Fig. 3, a, b, c, d). La caisse est construite en bois de chêne taillé sur quartier. Elle comporte deux parois verticales extérieures et deux montants intérieurs. Ces derniers se prolongent dans le haut et délimitent la partie surélevée. Ces montants sont ancrés à queue d'arondes dans l'élément horizontal formant la base. Dans le haut, diverses planches disposées en appentis assurent la cohésion de l'ensemble. Ces divers éléments sont assemblés au moyen de solides queues d'arondes.

L'arrière de la caisse est constitué de planches grossièrement embrevées les unes dans les autres. La rive plus fine (celle proche du coeur) s'emboîte dans une entaille sommaire pratiquée dans la rive plus épaisse de la planche suivante (rive proche de l'aubier). Ce "plancher" un peu sommaire est consolidé au moyen de deux barres de renfort chevillées dessus. Ces barres contribueront à maintenir la cohésion de la caisse lorsque celle-ci sera soumise à la traction du poids des volets. Ce "plancher" est solidement fixé à la caisse au moyen de chevilles implantées sur tout son pourtour. Il rappelle certains planchers qui ont servi à supporter les plus anciennes peintures sur toile, comme celui de *Jésus chez Marthe et Marie*, (Bruges, Hôpital S. Jean, inv. OSJ 6771).

Les trois espaces verticaux de la caisse sont divisés par des plateaux horizontaux: un plateau central légèrement surélevé par rapport aux deux plateaux latéraux. Ces plateaux ont une double fonction: celle de porter les sculptures, mais en même temps, d'assurer la solidité de la caisse et de la maintenir d'équerre. Grâce aux petites consoles sculptées à gauche et à droite, le plateau central s'appuie sur les plateaux latéraux. Ainsi est assurée la cohésion structurelle des trois plateaux.

Le montant intérieur gauche comporte des marques à la gouge. Des marques de ce type ont été observées au revers de panneaux peints, sur un socle de sculpture et sur un autre retable [4] mais elles n'ont pas à ce jour reçu d'interprétation. Nous pensons que, dans le cas présent, on pourrait l'expliquer comme suit: "ceci est un montant" (trait vertical), "qui doit recevoir un plateau" (trait horizontal), "qui doit venir s'implanter à cet endroit" (trait oblique). Sous le plateau la marque est complétée par une indication du même genre. Ces marques à la gouge auraient alors la signification de marques d'établissement [5]. Lorsqu'elle se retrouve au dos de panneaux peints, elle signifierait alors simplement le emploi d'un bois précédemment destiné à un autre ouvrage. Ce emploi pourrait alors impliquer une relation entre les "huchiers" et les "menuisiers" qui préparent les supports de peintures. S'ils disposaient des mêmes planches, cela semblerait signifier soit que les mêmes artisans ont construit la huche destinées à contenir les sculptures et les volets destinés à être peints, soit qu'ils travaillaient au moins occasionnellement dans le même atelier.

Un bois cintré est alors mis en place dans la partie haute centrale. Il s'appuie sur un évidement pratiqué dans les montants centraux. On taille dans ce bois cintré la partie haute de la grande gorge (ou voussure). D'autres bois sont alors mis en oeuvre; ils prennent appui sur l'entaille pratiquée dans les parois extérieures. Ces bois sont moulurés là où ils jouxtent la peinture. Ils serviront surtout de support sur lequel sera chevillé la dernière partie du cadre, la grande corniche qui surplombe le retable. Latéralement cette corniche est chevillée directement sur les parois extérieures dont la hauteur débordait légèrement la caisse.

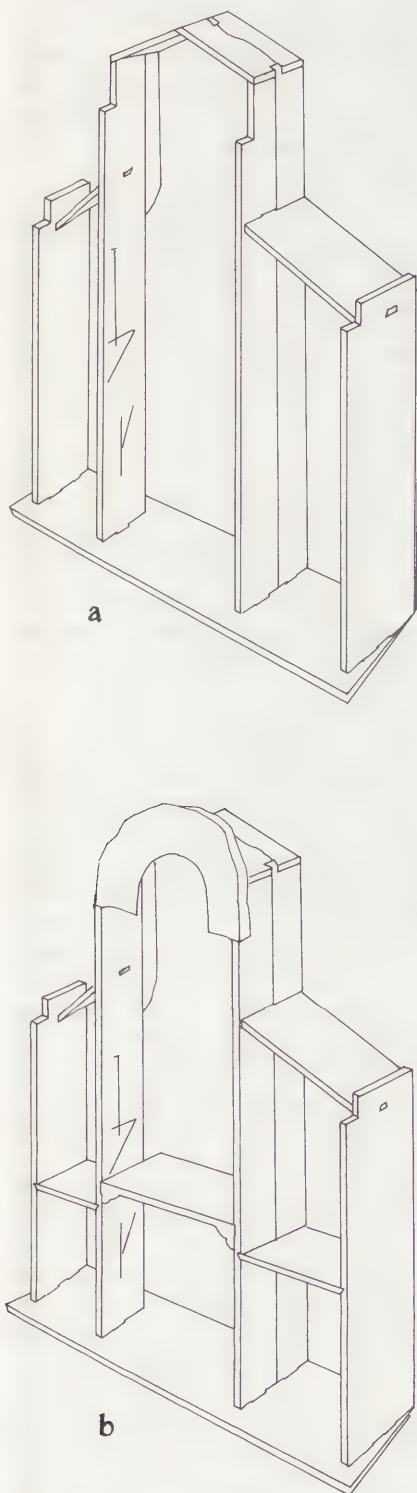


Fig. 3. Les étapes de la construction de la huche du retable d'Herbaix sous Piétrain.

L'examen des profils et de la polychromie du cadre donnent les résultats suivants. Le cadre est à doucine et à talus; la traverse inférieure n'est pas moulurée. La polychromie du cadre extérieur est noir et or; le cavet de la doucine est bleu. Il y a deux étapes distinctes dans la polychromie de la huche. Une assiette rouge-vif supporte la feuille d'or qui décore la caisse vide (cadres et plateaux, y compris les petites consoles à tête de mort). Dans les éléments sculptés qui constituent le "remplissage" de la caisse, l'assiette de la dorure est pâle. La voussure centrale dans le haut, bien que faisant partie structurellement de la caisse, est laissée à la seconde étape de la polychromie et la dorure y est posée sur assiette pâle. Ce fait atteste bien de la répartition en deux étapes au moins de la polychromie de la partie centrale du retable. Un fond noir est largement brossé sur le fond de la caisse, aux emplacements qui seront recouverts d'un remplage ajouré.

Les volets

La menuiserie des volets est semblable à celle généralement observée dans les peintures de l'époque. Les assemblages des éléments du cadre se font à enfourchement; ils sont chevillés. A l'intérieur des volets, les surfaces sont divisées par deux traverses. Dans le bas une petite latte chevillée sur le panneau et embrevée dans les montants, divise les surfaces en harmonie avec la partie centrale. Cette petite latte reçoit une mouluration semblable à celle donnée au plateau de la caisse, mais il faut remarquer que le développement de la moulure n'a pas la même ampleur dans l'un et l'autre cas. Ceci est lié à l'épaisseur des bois mis en oeuvre, épaisseur qui est à son tour liée à la fonction que les bois ont à jouer. Le petit compartiment haut des volets est constitué d'un support indépendant. La traverse du cadre qui l'amorce est donc un élément doublement rainuré. Sa présence s'explique peut-être pour des raisons iconographiques, mais probablement essentiellement pour des raisons fonctionnelles. Elle contribue à maintenir la menuiserie d'équerre et divise le support dans la hauteur. Elle supporte et maintient les planches les plus déjetées de la construction, celles dont le poids risquent le plus de générer des tensions. Cette petite traverse répond à la barre de renfort chevillée au revers du plancher. La seule exigence iconographique ne suffit pas pour expliquer cette construction. En effet le compartimentage de la surface pouvait se faire picturalement. Les zones inférieures de l'intérieur des volets portant chaque fois deux scènes, à gauche, l'Annonciation et la Visitation, à droite, la Présentation au temple (?) et la Fuite en égypte sont séparées par une seule colonnette peinte et sans élément en relief.

L'examen des profils et de la polychromie des cadres donne les résultats suivants. Comme pour la caisse centrale, les cadres des volets sont à doucine et à talus dans la traverse inférieure. Au revers les cadres sont à talus. La polychromie des cadres des volets est refaite. A la face, elle est noire et or; le cavet de la doucine est bleu. Au revers la polychromie est noire. Cette disposition des couleurs reprend peut-être la disposition originale. Seule une observation au microscope (nous n'avons pas pu la faire) permettrait d'observer l'assiette de la dorure et de voir si elle a une relation avec l'une ou l'autre des deux étapes de dorure observées dans la huche.

Les éléments métalliques

Deux charnières de chaque côté supportent le poids des volets. Les lames sont entaillées (disposées dans une entaille pour en contrarier tout mouvement éventuel). Comme il est de règle, la partie portante comporte le plus grand nombre de charnons. On peut voir en outre que le serrurier avait disposé de larges pentures qui devaient renforcer la cohésion entre les parois latérales et le plancher arrière. Il y avait deux ferrures sur chaque côté. Celles-ci ont été enlevées.

Conclusion

La menuiserie raffinée des volets, aux assemblages à enfourchement et tenon et mortaise parfaitement ajustés, est très différente de la menuiserie à gros tenons et mortaises, fortes chevilles et solides queues d'aronde de la huche. Il est logique de suspecter un artisan différent. Toutefois la fonction spécifique de chaque partie du retable peut suffire à expliquer les différences. La menuiserie de la

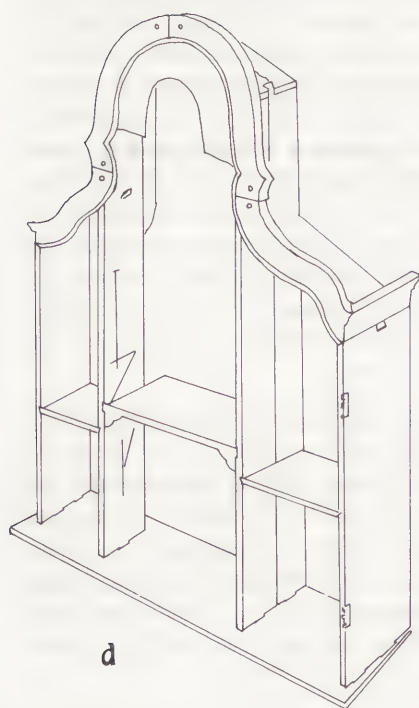
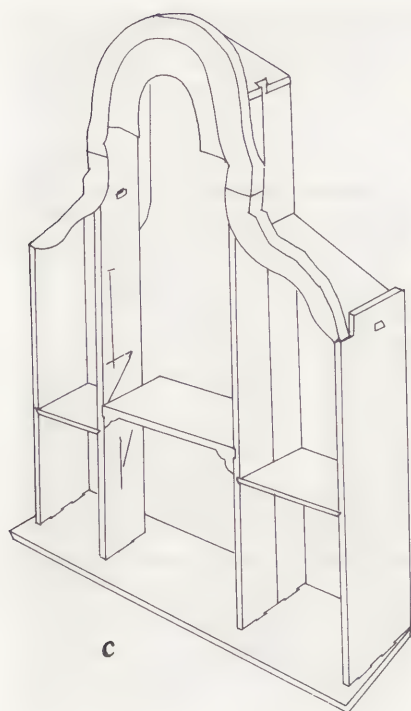


Fig. 3. Cont.

caisse serait entièrement camouflée, celle des volets apparente. Les formes chantournées des volets sont parfaitement jointives avec celles de la caisse et permettent une fermeture harmonieuse. Le souci de maintenir l'ensemble d'équerre se voit dans la construction de la caisse comme dans celle des volets et on peut dire que la conception de l'ensemble est parfaitement cohérente.

Il faut souligner que l'on retrouve dans la caisse deux éléments que l'on a observé par ailleurs dans la construction des supports de peintures indépendantes: les planchers qui soutiennent certaines toiles sont construits comme le fond de la caisse. Les marques à la gouge, qui n'avaient pas de sens au dos des supports de peintures, pourraient ici prendre une signification de marques d'établissement. Elle seraient alors, dans le cas des peintures, liées à un emploi dans un atelier. Il y a là des raisons de lier fortement la construction du support des caisses à celle du support des peintures.

Le retable d'Oplinter présente un plus large développement que le retable de Herbais. Il a subi quelques transformations au cours des temps. Le recouvrement original de la prédelle a disparu; l'extrémité supérieure des volets manque à la suite de la "modernisation" de l'oeuvre intervenue probablement à la fin du 16e siècle. Malgré ces différentes modifications, on peut observer que dans les grandes lignes ce retable anversois qui date de la même période que le retable anversois d'Herbais, est construit selon les mêmes principes.

Références

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5. Etablissement (marques d'): signes conventionnels qui permettent d'indiquer la position des pièces sur les bois à débiter, d'indiquer les parties qui seront assemblées et celles qui seront moulurées. néerl: kabelmerken; all: Bezeichnung des Holzes.

Working Group 20

Glass, Ceramics and Related Materials

Verres, céramiques et matériaux apparentés

1111

Résumé

On présente, en un compte rendu succinct, la restauration fondamentale d'un des principaux vases grecs à figures noires du Musée du Louvre, qu'on pourra rapprocher de la récente restauration du dinos de Sophilos menée au British Museum. Une étude scientifique et historique a d'abord permis d'éclairer le passé du dinos (ancienne collection Campana) et de poser le diagnostic nécessaire à sa conservation. Le traitement, articulé en deux temps (dérestauration/restauration) a dû prendre en compte une problématique complexe, du fait de l'état lacunaire du vase, notamment du pied, et des dégradations irréversibles causées par les pratiques abusives du 19^{ème} siècle. De nouvelles méthodes ont été expérimentées pour l'enlèvement des repeints à l'huile et le remontage du pied. Au terme de l'intervention, l'oeuvre antique a retrouvé sa physiologie originale.

Mots Clés

Dinos, Peintre de la Gorgone, Louvre, céramique grecque archaïque figures noires, Sophilos, collection Campana, histoire des restaurations 19^{ème} siècle, dérestauration, restauration



Fig. 1 : Le dinos du Peintre de la Gorgone (Louvre E 874) avant restauration.

La restauration du dinos du Peintre de la Gorgone au Musée du Louvre

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Introduction

La prestigieuse collection de céramique grecque du musée du Louvre comporte un certain nombre de pièces exceptionnelles; parmi elles figure un vase monumental (inventaire E 874), entré au Louvre en 1863, lors de l'acquisition de la collection Campana et composé de deux éléments indépendants: un grand bol sans anses (dinos) posé sur un pied haut, mouluré (Fig. 1). Considérée depuis le siècle dernier et, selon l'expression d'Edmond Pottier, comme "l'un des plus beaux spécimens de la céramique grecque archaïque" (1), l'oeuvre est attribuée à un maître anonyme, le "Peintre de la Gorgone", qui dirigeait l'un des principaux ateliers céramiques d'Athènes dans les années 600-580 avant J.C. (2).

Le vase retient immédiatement l'attention, tout d'abord par ses dimensions (hauteur totale 0,93m, circonférence maximale du bol 1,75m) et par la qualité remarquable du travail de poterie. Il s'agit à l'évidence d'un vase d'apparat, qui servait, de même que les cratères, à mélanger le vin et l'eau. On admire ensuite la richesse de la décoration peinte dans la technique de la figure noire, associant une scène figurée de style attique (meurtre de Méduse par Persée poursuivi par les Gorgones, et combat de guerriers) à des frises d'animaux et d'ornements d'influence corinthienne. Rares sont les dinoi archaïques de cette qualité qui nous soient parvenus, aussi bien conservés. Et lorsqu'on parle du dinos du Louvre, il faut aussitôt évoquer le célèbre dinos de Sophilos conservé au British Museum, dû à un artiste qui a peut-être été l'élève du Peintre de la Gorgone et qui, lui, a signé son oeuvre (3).

En 1984, le Département des Antiquités Grecques Etrusques et Romaines décida d'entreprendre une nouvelle restauration du vase (4). En effet des recherches menées par F. Villard avaient permis d'identifier, parmi les séries de tessons isolés conservés en réserve, un groupe de cinq fragments appartenant au dinos E 874 (dont un fragment important donnant le bras et le pied droits de Méduse). Il convenait donc de les insérer à leur place en modifiant, au moins ponctuellement, la présentation antérieure qui datait du 19^{ème} siècle. Mais bientôt on conclut à la nécessité d'une restauration fondamentale. L'opération s'achève aujourd'hui et il a paru intéressant de présenter dès que possible le résultat de ces travaux, d'autant plus que, par une heureuse coïncidence, le British Museum menait à bien de son côté une nouvelle restauration du dinos de Sophilos et y consacrait une publication toute récente (5). On pourra de la sorte comparer la problématique et la méthodologie de la restauration des deux vases.

L'histoire du vase et de ses restaurations à l'époque moderne

Sous le sceau de la collection Campana

Le dinos a fait partie au 19^{ème} siècle de la célèbre collection Campana. Exhumé sans doute lors des fouilles menées par le marquis dans la nécropole étrusque de Caere dans les années 1840-1850, il a dû être restauré à Rome, puisqu'il est décrit de manière implicite en tant que vase complet dans les *Cataloghi del Museo Campana* parus en 1858 (6). Mais à quel(s) restaurateur(s) fut-il confié ? On l'ignore. S'agirait-il d'un des deux frères Pennelli ? Rien ne permet d'affirmer pareille hypothèse à l'heure actuelle (7).

Le dinos subit ensuite les tribulations bien connues de la collection Campana, et il fit partie du lot de 11835 oeuvres achetées par le gouvernement français en mai 1861. Il dut voyager de Rome à Paris dans l'une des caisses apprêtées par l'emballeur français Espirat et il fut exposé au Palais de l'Industrie sur les Champs-Élysées, dans le cadre du Musée Napoléon III inauguré le 1^{er} mai 1862.

On en a en effet expressément mention dans la courte notice que le céramologue J. de Witte a consacré aux vases antiques du musée: le dinos y figure, toujours dans la série des "vases corinthiens", au nombre des exemplaires les plus remarquables, et si la brève description qui en est faite ne comporte aucune allusion à son état de conservation, c'est bien parce que, dans le langage du temps, il ne peut s'agir que d'un vase restauré, qui plus est de manière totalement illusionniste (8).

Mais la création du musée Napoléon III conçu comme "un musée d'art industriel" et ressenti par certains comme un rival potentiel du Louvre suscita une violente polémique. Les adversaires du projet l'emportèrent, et dès 1863, la collection était démembrée entre le Louvre et les musées de province. Le dinos E 874 resta au Louvre et prit place dans la grande galerie d'exposition de la céramique grecque, connu désormais sous le nom de "galerie Campana". Les mentions et illustrations qu'on en a par la suite prouvent que son état de présentation n'avait pas été modifié (9). Et il demeura ainsi, mis à part quelques reprises mineures opérées au 20ème siècle (recollages ponctuels à la gomme laque par exemple), jusqu'à l'intervention actuelle.

L'étude des restaurations du 19ème siècle

Bien des vases grecs du Louvre, provenant d'anciennes collections privées formées au 19ème siècle, ont été dérestaurés au 20ème siècle, sans qu'on ait toujours cherché à analyser et documenter les restaurations des siècles passés. Comme par ailleurs les archives muséales sont pauvres en témoignages écrits sur l'histoire de la restauration des antiquités, on conçoit d'autant mieux combien il importe d'étudier directement sur les oeuvres les derniers vestiges matériels des opérations de conservation, de restauration, de moulage etc. . . menées par nos prédécesseurs.

Ici on avait la chance de pouvoir travailler sur l'un des vases majeurs de la collection, ayant conservé quasiment intacte sa physionomie des années 1850. Et la première phase de l'intervention consista donc à rassembler un dossier d'examens et d'analyses scientifiques ainsi qu'une documentation photographique aussi complète que possible (examens et prises de vue en lumière naturelle, sous ultra-violet et infra-rouge; analyses des anciens matériaux de restauration: produits de bouchage, repeints, vernis; radiographie du pied afin d'étudier la technique antique d'assemblage et le système de remontage utilisé au 19ème siècle).

On put en tirer plusieurs conclusions, parmi lesquelles:

—Les matériaux employés étaient dérivés de la restauration des tableaux (à l'exception de l'emploi de terre cuite moderne pour restituer des tessons manquants). Le vase fut perçu avant tout comme un tableau peint sur terre cuite, et la matérialité du support céramique comptait finalement assez peu. Il y a donc un contraste étonnant entre la "manière forte" utilisée pour le remontage du dinos, à coups de scie, de râpe et de lime pour venir à bout de la matière rebelle, dans le cas de ressauts ou d'assemblages difficiles, et la "manière fine" dont témoigne la réintégration du décor peint. Sur ce point, l'illusionnisme menait parfois à des erreurs involontaires et cocasses: alors que le Peintre de la Gorgone avait égayé ses frises d'animaux de lions et de panthères bien différenciés, le pinceau fantaisiste des restaurateurs fit surgir des monstres hybrides, mi-panthère mi-lion (Fig. 2).



Fig. 2 : Exemple de repeint erroné du 19ème siècle (amalgame tête de panthère/corps de lion).

—L' "idéologie" de l'intervention était également ambiguë: il fallait recréer un original prétendument intact (d'où le maquillage extensif de la surface), mais aussi conserver un certain "cachet" d'authenticité archéologique (badigeon à l'intérieur du bol d'une couche de terre, simulant des dépôts d'enfouissement). L'intérêt mercantile et l'aspect "oeuvre de faussaire" des réparations du 19ème siècle, notamment Campana, ont déjà été abondamment soulignés. Mais n'oublions pas non plus l'équivoque de la restauration telle que la définissait Viollet-le-Duc en 1863: "rétablir ce qui peut n'avoir jamais existé" (10).

Etat de conservation du dinos et diagnostic

On mena également une série d'analyses sur les matériaux antiques constituant le vase (pâte céramique, restes de rehauts pourpres).

Des tests de dérestauration montrèrent enfin la nocivité de certains des anciens matériaux de restauration: l'acidité et l'hygroscopicité des adhésifs et des enduits de bouchage, à base de colles animales et de blanc de Meudon, provoquaient une desquamation parfois sévère de la terre cuite. L'altération prononcée des repeints à l'huile constituait un autre facteur de dégradation, chimique et chromatique, de la surface. Enfin le remontage du pied présentait des signes évidents de fragilisation, notamment dans la zone du balustre (partie médiane renflée entre deux tores saillants).

Le diagnostic s'imposait donc de lui-même. Une intervention partielle n'eût abouti qu'à une présentation hybride, chaotique et chancelante. Il fallait reprendre totalement la restauration.

Dérestauration: démontage et nettoyage

Démontage

Le bol fut démonté en une seule opération, par immersion dans de l'eau tiède qui permit le gonflement et la dissolution partielle des anciennes colles animales.

Par contre, on démonta le pied progressivement: on dégagait d'abord la zone du balustre où l'on mit en évidence la complexité du système de remontage confectionné au 19^{ème} siècle, en partie décelé sur la radiographie (anneau en terre cuite moderne fixée par des tiges de bois et par un collage à la gomme laque au dessous de la vasque (Fig. 3), coque en stuc épousant la forme interne du balustre et remploi d'un tesson antique). Puis on démonta le haut et le bas du pied.

Nettoyage

Cette phase du travail fut extrêmement longue et complexe. Elle s'effectua en six étapes:

1 à 4: élimination des anciens vernis, repeints, mastics et adhésifs. L'enlèvement des repeints s'avéra particulièrement difficile; un dégagement mécanique était exclu dans les nombreux cas où le repeint était appliqué directement sur la terre cuite antique. Et la plupart des solvants usuels (diméthylformamide par exemple) se révélaient inefficaces. Au terme de nombreux essais, on mit au point une solution de nettoyage à base de tertio-butylamine et d'acétate d'éthyle (50/50) qui permit de dissoudre suffisamment les repeints sans devoir frotter ni risquer d'abimer de ce fait l'épiderme argileux sous-jacent (11).

5: nettoyage des incisions détaillant l'intérieur des figures noires.

6: à ce stade, la dérestauration était achevée. Était-on alors de retour à un "degré zéro", au stade initial conçu par le Peintre de la Gorgone? Non, car la dimension archéologique de l'oeuvre marquée par l'enfouissement réapparaissait sous la forme de dépôts et de concrétions que les restaurateurs Campana s'étaient contentés de dissimuler plutôt que de les éliminer. Après analyse, on décida tantôt de laisser subsister ces marques (cas par exemple de concrétions siliceuses trop dures pour être dégagées sans danger pour le vase), tantôt de les atténuer lorsqu'elles gênaient la lecture du décor peint (cas de dépôts noirs de nature organo-métallique, traités avec de l'acide mercaptoacétique).

Restauration: Remontage et réintégration

Remontage

Composé de 58 fragments donnant l'intégralité du profil et relativement peu lacunaire, le bol a pu être remonté sans difficultés majeures en employant des colles cellulose solubles dans l'acétone (Uhu-extra et Uhu-hart).

Par contre, le remontage du pied posait de redoutables problèmes. A l'origine, le pied devait supporter intégralement le poids du bol (environ 7 kilos, à vide). Or la partie médiane du pied (balustre) était très sévèrement endommagée: du fait de l'absence de tessons originaux aussi bien que des brutalités commises par la restauration Campana (sciage de la partie inférieure de la vasque et de la partie supérieure du fût), le balustre "flottait" dans le vide, et ne présentait plus aucun point de jonction avec les parties hautes et basses du pied. Comment donc recréer techniquement l'unité et la stabilité de l'ensemble?

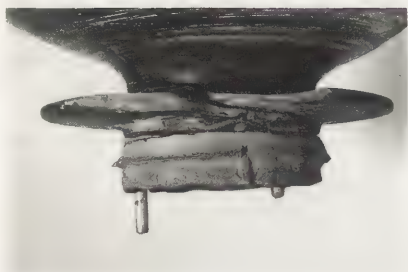


Fig. 3 : Le pied en cours de démontage : anneau en terre cuite moderne fixé à la vasque qui a été sciée (restauration Campana).

Sans entrer dans le détail des opérations qui déborderaient du cadre de ce rapport, on soulignera les grands principes qui ont guidé l'intervention:

—souti de la conservation à long terme de l'original, en introduisant le moins possible de matériaux synthétiques au contact direct avec la terre cuite antique.

—recours à un système de support interne, passant par l'axe creux du pied, pour supporter l'essentiel du poids du bol. C'était le principe déjà adopté par les restaurateurs du British Museum pour le remontage du dinos de Sophilos.

—souti de conserver une certaine mobilité d'assemblage, de manière à pouvoir aisément manipuler l'objet ou modifier éventuellement la présentation.

En pratique, on a commencé par recoller, avec les mêmes colles que pour le bol, les 43 fragments conservés du pied, de manière à recomposer trois ensembles distincts: la vasque, le balustre, et le fût avec le plat du pied. Puis on a confectionné le support interne, en bois et en métal. Est venue ensuite la phase la plus délicate de l'opération, à savoir le raccordement du balustre au fût et à la vasque. Pour ce faire, on a étudié soigneusement les caractéristiques technologiques et stylistiques du dinos, afin de proposer la reconstitution la plus plausible quant à:

—la hauteur et le profil à restituer dans le haut et le bas du balustre, lacunaire

—le centrage et l'horizontalité des différents éléments par rapport à l'axe de façonnage du pied

—la coordination des frises ornementales superposées qui décorent le pied. En étudiant le vase, on a pu mettre en évidence l'existence sinon d'une véritable "face principale", du moins d'un angle de vue privilégié dans l'organisation du décor peint. Le positionnement des différents éléments a été effectué en conséquence (Fig. 4).

Outre le fait que ces recherches ont nourri une meilleure connaissance de l'oeuvre, elles ont aussi révélé deux faits marquants: 1°) les restaurateurs du 19ème siècle avaient utilisé, pour fixer le balustre au fût, un fragment de vase antique qui s'est révélé étranger au dinos. 2°) ils avaient inversé le sens du balustre, prenant le haut pour le bas. L'erreur a pu être détectée notamment grâce à l'étude de la forme du balustre, légèrement déformée et affaissée sous le poids de la vasque, avant la cuisson du vase.

Réintégration

Pour la nouvelle présentation du vase, on a choisi de suivre un parti clairement archéologique, en effectuant un bouchage très légèrement en retrait dans les zones de comblement et en ne retouchant pas le réseau de cassures qui reste donc apparent (Fig. 5).

Plusieurs raisons expliquent ce choix: 1°) le remontage du balustre peut comporter une légère marge d'erreur, en dépit des recherches et des efforts déployés. C'est une proposition de restauration, et elle doit se lire en tant que telle. 2°) comme on l'a dit, l'état général de surface du dinos a énormément souffert des abus des restaurations passées (bords des tessons limés, vernis noir arraché, incisions détaillant les figures disparues etc. . .). Pour réintégrer tous ces accidents, il eût fallu mastiquer et repeindre à nouveau, de manière jugée trop extensive par les conservateurs et les restaurateurs.

La "cire de Florence", matériau de bouchage utilisé depuis plusieurs années pour la restauration de vases grecs du Louvre ne convenait pas du tout dans le cas du dinos; en effet, elle s'imprégnait dans la pâte céramique tendre et poreuse, et provoquait la formation de taches. Le comblement des lacunes et des cassures fut donc opéré au moyen de plâtre. Une première couche de plâtre dentaire blanc (Vel Mix Stone), fut recouverte en surface d'une seconde couche de plâtre pigmenté dans la masse (plâtre Molda 3 + pigments minéraux en poudre + émulsion acrylique AC 33).

Enfin, dans toutes les zones de comblement, une retouche peinte à l'acrylique uniformisa la coloration du matériau de bouchage au ton de la terre cuite.

Pour protéger le fragile épiderme du vase, on procéda à une consolidation de surface (Paraloid B 72 dissous à 2% dans du toluène).

Pied du dinos du Peintre de la Gorgone. L.R.4
support interne

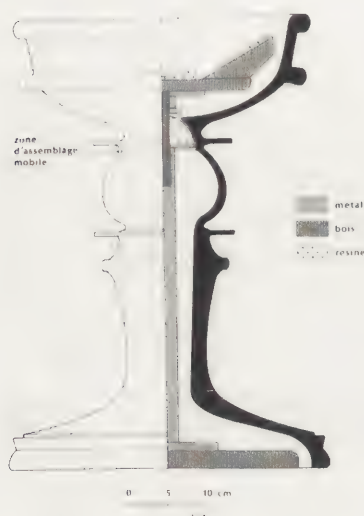


Fig. 4 : Dessin du pied restauré : profil du vase et du support interne.



Fig. 5 : Le dinos après restauration.

Conclusions

Au terme de cette longue entreprise qu'a été la restauration du dinos du Peintre de la Gorgone, quel bilan retenir ? L'intervention a permis d'expérimenter de nouvelles méthodes de traitement (nettoyage des repeints huileux, technique de remontage du pied).

Exposée prochainement dans les salles rénovées du Grand Louvre, l'oeuvre a retrouvé son vrai visage. Ce qu'on apprécie désormais, c'est l'expression de la main du créateur antique, avec son talent personnel, ses singularités et ses imperfections. C'est le coloris original de la terre et du vernis noir attiques, et la ligne harmonieuse du pied, purifiée de ces empâtements et de cette incohérence que générait le remontage erroné du balustre.

Et si l'intervention actuelle a été aussi passionnante, c'est bien parce qu'elle a permis d'embrasser l'oeuvre dans la continuité de son histoire, de comprendre le lien entre la création originale du maître attique, le destin archéologique du vase, cassé, marqué par l'enfouissement, sa résurrection mais aussi sa métamorphose entre les mains des restaurateurs romains au service de Campana, et son état actuel. Même s'il nous manque encore bien des jalons dans ce récit, il n'en reste pas moins que cette dimension historique des collections d'un musée tel que le Louvre apporte un intérêt accru à l'étude et à la restauration des oeuvres, enrichit la problématique de leur sauvegarde et devrait permettre de retracer peu à peu l'histoire encore si mal connue de la restauration des antiquités au cours des siècles.

Notes

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Abstract

Two clays fired to 900°C were desalinated by the static immersion and stirred solution methods after having been impregnated with calcium acetate and consolidated with Acryloid B72, Tetraethyl Orthosilicate (TEOS), or Methyl Triethoxysilane (MTS). The rate and extent of salt extraction were monitored by Ionic Conductivity and Atomic Absorption Spectroscopy (AAS).

Keywords

Ceramic, salt, desalination, consolidation, archaeological, Acryloid B72, Tetraethyl Orthosilicate, Methyl Triethoxysilane, Ionic Conductivity, Atomic Absorption Spectroscopy, calcium acetate, silane, acetic acid, storage, wood

The Consolidation and Desalination of Ceramic Impregnated with Calcium Acetate

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Introduction

The purpose of simulating salt-contaminated archaeological pottery was to test the efficiency of two desalination methods and the effect of three consolidants on the release of salt. Calcium acetate $\text{Ca}(\text{CH}_3\text{COO})_2$ was chosen since several salts containing this compound have been identified in the efflorescences on pottery and other inorganic objects (1,2,3). The formation of these salts in the references cited occurred in wooden storage materials in which the source of acetate is attributed to the emission of acetic acid vapour from the wood. Similar desalination tests have been run using sodium chloride (4) and sodium sulphate (5).

The clays were chosen to simulate those used in the Mediterranean world in antiquity. Both clays contained the common clay minerals illite, kaolinite and montmorillonite but differed in calcium and iron content. The earthenware clay was obtained commercially in Toronto, Ontario, Canada and the calcareous clay derived from Crete, Greece. The firing temperature of 900°C fell within the range used for pottery in the ancient Mediterranean.

Test Preparation

After firing the clay tiles in an oxidizing atmosphere at 900°C for 30 minutes, they were impregnated with a 1.5 M solution of calcium acetate under reduced pressure of approximately 22 mm Hg (6). The TEOS was prepared as a volume solution of 60% TEOS, 32% ethanol (95%), and 8% HCl (1% vol/vol aqueous solution) (7). The MTS was prepared in the proportion 1 ml MTS to 0.135 ml 0.1 N HCl under agitation (8). The same vacuum impregnation technique was used to introduce TEOS and MTS into the salt-laden tiles. The Acryloid B72 was introduced in the tiles as a 10% solution in acetone (wt/vol) by capillary absorption in a covered chamber to retard solvent evaporation.

Consolidants

A consolidant is required for those ceramic objects which have been weakened by soluble salt activity so that they may be desalinated. The open pore volume and open pore distribution of the object will influence the quantity of consolidant deposited. Theoretically, the consolidant reduces the open pore volume thereby reducing the rate of water passage and subsequently the rate of desalination.

Acryloid B72, a methacrylate-ethyl methacrylate copolymer, was chosen for its long-term stability and its successful adoption by many conservators as a consolidant in various porous materials. The acrylic resin is deposited on the surface of the pore walls and capillaries upon evaporation of the solvent carrier and allows the passage of water vapor in porous objects. The degree of bulking of the pores by the resin regulates the passage of liquid water.

Tetraethyl Orthosilicate (TEOS) $(\text{Si}(\text{OC}_2\text{H}_5)_4)$ and Methyl Triethoxysilane (MTS) $(\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3)$, both alkoxysilanes, have found frequent application as consolidants for salt-contaminated stone. Polymerization, which is initiated by water, occurs by hydrolysis and condensation (9). The amorphous silica deposited in the pores reduces the open pore volume, retards the penetration of moisture, and increases hardness (10). Both silanes allow the passage of water vapor in porous objects. The presence of methyl groups in MTS provides greater water-repellency. MTS has been tested previously as a consolidant (11) and as a water-repellent (12) for ceramics. TEOS, as a consolidant in salt-contaminated limestone, has been shown to allow the migration of salt (13). The porosity,

water absorption and permeability were reduced in salt-laden brick which was consolidated with the alkoxysilanes (14).

Physical Properties and Weight Gains of the Ceramic Tiles

The weight gains (%) were determined gravimetrically. The greater weight gains made with salt impregnation by the calcareous ceramic (Table I) are

Table I. Weight gains (%).

	Calcareous ceramic			Earthenware ceramic			Desal method
	w/salt	w/con	Product yield	w/salt	w/con	Product yield	
Control	6.35			4.15			si
	7.13			3.61			ss
w/TEOS	6.01	0.20	10.53	4.45	3.10	19.62	si
	6.70	0.03	7.70	4.41	3.02	19.21	ss
w/MTS	5.41	2.23	27.94	4.38	5.27	100	si
	5.43	3.82	33.33	4.39	5.05	34.57	ss
w/Acry	13.47	-0.80		4.85	3.07		si
	11.12	-0.03		4.70	3.02		ss

con = consolidant; ss = stirred solution; si = static immersion.

Table II. Physical properties of ceramic test tiles.

Tiles	Apparent porosity P%	Liquid absorption A%	
Earthen	31.49	17.30	control
Calcar	33.82	18.44	
Earthen	16.24	7.37	w/salt
Calcar	7.71	3.43	

earthen = earthenware ceramic; calcar = calcareous ceramic.

supported by the greater porosity and absorption capacity of this ceramic (Table II). The greater reduction in both physical properties by salt impregnation explains the smaller weight gains made by the calcareous ceramic with TEOS and MTS. Some salt may have formed a crust on the surface of the calcareous ceramic which prevented the penetration of the Acryloid in these tiles. The small weight gain made with TEOS by this ceramic might also be attributed to a salt-crust formation.

The product yield (Table I), as the quantity of silica deposited in the tiles, was determined with this formula:

$$\frac{c - a}{b - a} \times 100 = \% \text{ product yield}$$

where a = mass of ceramic, b = mass of ceramic + wet consolidant, c = mass of ceramic + cured consolidant.

The product yield obtained with MTS fell short of the reported maximum yield of 37.6% (15) in all groups with one exception. The excessive yield in one test may be due to incomplete curing or gravimetric error. The product yield obtained with TEOS exceeded the reported maximum yield of 16% (16) in the earthenware groups but fell short of the maximum in the calcareous groups. The excessive yields may be attributed to incomplete curing of the resin or incomplete evaporation of the solvent carrier.

Methods of Desalination

In the static immersion method, the ceramic tiles were placed on a layer of glass stirring rods resting on the bottom of a beaker to allow circulation of solution around the tiles. In the stirred desalination tests, the tiles were suspended in a teflon-coated fiberglass mesh which allowed solution circulation around the tiles. A magnetic stirrer maintained constant movement of the solution. Both methods were tested at room temperature. The ionic conductivity in $\mu\text{mhos/cm}$ ($\mu\text{siemens/cm}$) of the desalination solution was measured every 2 hours over an 8 hour period daily for the duration of 5 days (104 hours total) (Table III). A Fisher Scientific Conductivity Meter, model 09-330, was used. The solution was monitored, then replaced with new deionized water, twice daily at the start and finish of the 8 hour day. The conductivity of the solutions were totalled to derive the total ionic conductivity of each desalination test (Table III). The first and last extractant solutions of all tests were kept for analysis of calcium (Ca ppm) by Atomic Absorption Spectroscopy (Table IV). A Perkin-Elmer 2380 Atomic Absorption Spectrophotometer was used.

Table III. Ionic conductivity ($\mu\text{mhos/cm}$).

Hours elapsed	Static immersion				Stirred solution			
	Salt	TEOS	MTS	Acry	Salt	TEOS	MTS	Acry
Calcareous ceramic								
2	700	1174	1164	1482	2300	1207	1408	1352
4	280	536	338	245	80	615	308	525
6	440	151	145	46	21	214	123	158
8	160	180	144	28	26	235	140	185
24	72	72	61	6	13	99	64	86
48	80	94	74	5	15	145	79	110
72	60	51	39	3	13	67	49	53
96	80	65	58	2	21	99	69	90
104	60	32	27	2	11	50	39	52
Earthenware ceramic								
2	1100	1257	1440	1482	1000	1462	1347	2326
4	40	236	73	245	40	214	77	286
6	44	28	24	46	12	19	27	38
8	12	13	37	28	7	8	36	23
24	8	4	14	6	5	4	15	4
48	7	14	38	5	5	6	23	4
72	8	2	9	3	4	3	13	2
96	8	3	32	3	5	4	20	2
104	9	2	11	2	4	3	9	2
Total conductivities (in $\mu\text{mhos/cm}$)								
Earthenware ceramic					Calcareous ceramic			
	si	ss			si	ss		
w/salt	1236	1082			1932	2500		
w/TEOS	1559	1723			2355	2731		
w/MTS	1678	1567			2050	2279		
w/Acry	1820	2687			1819	2611		

si = static immersion; ss = stirred solution.

Table IV. Atomic absorption spectroscopy results (Ca ppm).

Hrs elapsed	Control	Salt only	TEOS	MTS	Acry	Desal method
8	0.9	146.3	206.3	249.99	281.3	si calcar
104	<0.4	8.0	6.5	3.46	11.3	si ceramic
8	1.3	177.1	212.5	288.45	250.0	ss
104	<0.4	9.9	7.8	5.38	7.0	ss
8	0.4	207.9	231.3	250.0	287.5	si earthen
104	<0.4	0.9	2.8	1.75	2.3	si ceramic
8	0.5	184.8	243.8	288.45	350.0	ss
104	<0.4	0.9	1.0	12.15	1.3	ss

si = static immersion; ss = stirred solution; calcar = calcareous; earthen = earthenware; desal = desalination.

Results

AAS confirms the presence of calcium in the last desalination solutions of all test groups with less calcium in the earthenware ceramic tests. This calcium could derive from calcium acetate or leached ceramic matrix. The smaller conductivities of the last desalination solutions from the earthenware ceramic indicate that more calcium acetate may have been removed than from the calcareous ceramic.

The rate of salt release was determined by calculating each conductivity reading as a percentage of the total conductivity which was plotted against hours elapsed. Since the calcareous ceramic produced similar curves for both desalination methods and likewise for the earthenware ceramic only one set of graphs is illustrated representing the static immersion method (Figures 1,2). The stirred solution method proved to be only slightly more efficient than the stirred method.

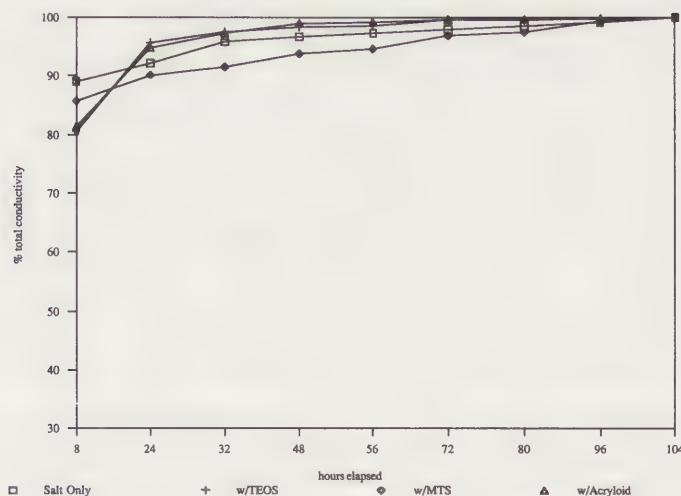


FIGURE 1 RATE OF SALT RELEASE—non-calcareous ceramic.

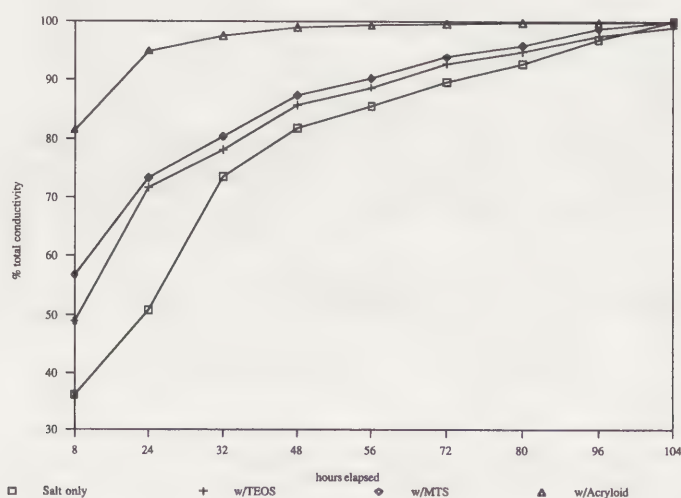


FIGURE 2 RATE OF SALT RELEASE—calcareous ceramic.

The major difference between desalination methods with the calcareous ceramic was that the salt from the unconsolidated tiles in the static immersion method was released more slowly than the salt from the consolidated tiles. In the stirred solution tests, the salt from the unconsolidated tiles was removed more quickly than that from the consolidated tiles which is what one would expect. This discrepancy has not been accounted for, although differences in the degree of penetration by the consolidant into the ceramic may play a role.

Comparing the consolidants in the earthenware ceramic tests, MTS retarded slightly the release of salt throughout the tests after the first desalination solution. The unconsolidated earthenware tiles were not the fastest to release salt as one would expect.

Comparing ceramic types, the desalination rate for the earthenware ceramic was considerably faster. This may be due to the greater porosity and greater absorption capacity of the salt-impregnated earthenware tiles although one might have expected a reduction in these capacities by the greater weight gains made with consolidants. Similar results were found using sodium sulphate (5).

Conclusion

Each of the three consolidants allowed the dissolution and release of the calcium acetate. The degree of consolidation achieved of salt-laden ceramic depends on the degree of unobstructed pores and interconnecting capillaries in the body of the object. It has been demonstrated that the obstruction of pores with calcium acetate hindered penetration of the TEOS and Acryloid in the calcareous ceramic. The two desalination methods proved to be of similar efficiency, the stirred solution method produced a slight increase in the rate of desalination. The tiles

containing MTS showed the slowest rate of salt release (after the first solution) in the earthenware ceramic. The hydrophobic properties of MTS were not apparent in the calcareous ceramic, however. The greater apparent porosity and liquid absorption of the salt-laden earthenware (as compared to the salt-laden calcareous ceramic) are reflected in the higher rate of desalination of this ceramic.

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Working Group 21

Training in Conservation and Restoration

Formation en conservation et restauration



Abstract

Training in conservation for a multicultural group, characteristic of ICCROM courses since 1964, is becoming common in many training programs. The experience is challenging for both the teachers and students. To ensure that the impact is positive requires a personal and pedagogical approach which is open and flexible. ICCROM has learned many lessons along the way. Sharing this experience presents an opportunity to further develop thinking, and to review and harmonize teaching approaches in the field of conservation.

Multicultural Training: A Rich Mosaic or an Impossible Puzzle?

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Introduction

In 1964, ICCROM welcomed its first group to an international course on conservation. Since that time, more than a hundred groups have followed - all with these characteristics: 12-20 participants, both male and female, from different nationalities (at least 10 represented each time), of different religions and cultures, with different educational backgrounds and varied professional experiences.

A rich mosaic or an impossible puzzle? The complex composition of the groups which participate in ICCROM programs, regardless of the programs' themes or objectives, put teaching approaches into question. For nearly thirty years now these problems have been encountered, and solutions have been proposed, tried out, abandoned or refined. This extraordinary pedagogical exercise is possible thanks to the collaboration of a large number of specialists who, beside their own work, teach regularly in ICCROM's programs.

At the same time, the field of conservation has changed considerably: international meetings have multiplied, national schools have grown, specialized and opened up more and more to foreigners; museums and institutes regularly open their laboratories and workshops to students from around the world. In this context, what was once especially characteristic of ICCROM courses is becoming common to some extent in the majority of training programs.

As both national and international institutes take on the challenges of teaching to multicultural groups, the organizers and teachers take on a responsibility which surpasses the transfer of scientific and technical knowledge: awareness and respect of differences in culture, religion and language become important considerations in the design and execution of training activities.

The multicultural group

In an international setting, it is impossible to put together a homogeneous group of participants. Working with such a mixed composition of personalities and backgrounds is both the beauty and the challenge of organizing ICCROM courses. The main challenge is ensuring that the all participants recognize and maximize the benefits of interaction with such a heterogeneous group of teachers and fellow participants.

Only a small percentage of participants (and also teachers) have previously had the chance to work or live outside their own country. Even fewer have been exposed to such a multicultural environment as the one offered by ICCROM. Working and interacting with or within a multicultural group is not an experience that benefits everyone. In fact, the impact can be negative for the unprepared student or teacher. That is why, even in the selection process, one needs to look for flexibility, empathy, mental openness and the ability to be objective.

As the teachers and organizers must understand the group, so too must those in the group understand one another. It is through this understanding that they will benefit from their experience and avoid the misunderstandings and conflicts which have a negative impact on the individual as well as the entire group. It is important for the organizers to understand their role in establishing a learning environment where 'cultural' conflicts can be avoided or resolved. By providing orientations and professional support to multicultural groups, the risks of misunderstanding, unresolved conflicts and intolerance are lessened while the chance for greater understanding and collaboration is increased.

We have learned that the individuals' personal security needs must be met (housing, food, health) before they will consider their studies or group interaction. Orientations to the city and people surrounding them in their new environment offer the first chance to bring them together. Too often, when people of different nationalities or cultural backgrounds meet, their previously held stereotypes and impressions are only reinforced. Contact between persons is not in itself a guarantee that mutual respect and understanding will follow.

Multicultural interaction can offer everyone a unique view of another culture's values and perspectives. By encouraging openness and tolerance, the exchange of ideas and creation of ties, both personal and professional, adds to the learning experience. At the same time, teachers and participants with fewer problems of integration and understanding are better able to concentrate on their studies and training (1).

Language—barrier or instrument of knowledge?

The absence of conservation terminology from one language is not always an indication of a lack of or a poor development of concepts. It may simply indicate a different approach to these concepts. Therefore, the exclusive use of a language (i.e. English) as the vehicle language is not as casual as it may appear to be.

At ICCROM, where English and French are the official languages, efforts have always been made to offer bilingual training and to avoid *la prédominance d'une langue* and the total reliance upon it by those who use it. In order to do this, the first solution attempted was simultaneous interpretation (from 1964-71) which turned out to be at odds with the initial objective. In fact, it reinforces division, impedes the interaction between teachers and participants and inhibits the teacher who does not have control of the translation/interpretation and thus cannot fully rely on his teaching methods.

Since 1971, the use of consecutive interpretation has resolved some of these difficulties because the translator is no longer a professional interpreter but a conservator who actively participates in the training. The teacher, whose teaching time is reduced by almost half, must therefore make a particular effort to organize information, prepare visual and written material, simplify the vocabulary (key words), and find bibliographic references in both languages.

Consecutive interpretation gave ICCROM the opportunity to develop and consistently improve teaching methods and materials, particularly all visual aids (projected images, slides, etc.) which can enhance or even replace the oral or written message. This extra effort has been compensated by the quality of the results and reactions of the participants, whose motivation and participation far excel those of participants in courses where simultaneous interpretation has been used.

Recently, for financial reasons and with the regionalisation of certain activities, ICCROM's bilingual approach has been progressively abandoned in favor of increased use of one language (English). *C'est très regrettable*; on the one hand, it limits the possibilities of access to training, and on the other, it contributes to a linguistic hegemony of conservation information, concepts and methodologies. In fact, bibliographic resources of the most widely diffused conservation publications are generally in English.

One can, in any case, wonder about the value of translation in a multicultural context. What about the languages used by the minorities within a group when one or even two languages are given privilege? How can we encourage the use of other languages and ways of thinking without negative consequences for the course content?

One of ICCROM's solutions was to offer a bilingual course . . . without translation (2)! This approach had interesting consequences for the behaviour of the participants and the course content. However, this system can work only when both the participants and the teachers know one of the languages well and can understand the other. Teaching takes place in one or the other language. The fact that everyone finds himself at different times in a position of strength or

weakness modifies the rapport within the group and facilitates interactions. It should be noted that the mother tongue of a large number of ICCROM participants is often a third language which, in such a setting, can sometimes be useful for comparison or as an additional communication tool.

Language differences may be the most obvious problem facing international training programs. However, even a common language does not eliminate other differences - differences, which if ignored, can have equally disruptive effects on training (national and international).

Entrer en relation avec la différence

Without lessening the importance of "giving the floor" to other languages, there are other means which can contribute to the transfer of knowledge. In particular, there are ways which attempt to integrate differences into the very design of training.

For instance, when using examples to elaborate an idea or concept, it is important to take into consideration the environment and values familiar to each element of the group; in a multicultural group you can be sure that an example using church, mosque, temple or shrine will evoke different responses from each individual. It is important to recognize different interpretations of key-terms or ideas (i.e. "antique" or "humid") and give alternatives when referring to sophisticated instrumentation. It is also important to verify that images, graphics and drawings effectively clarify the message.

Integrating differences into training requires specific preparation by both coordinators and teachers and often leads to structural changes in the course and in the course materials. The universal must be distinguished from the particular, the method from the recipe.

Learning together

Integrating differences can also be achieved by encouraging contributions and feedback from participants, thereby building the course together and providing opportunities for participants to learn from each other. Examples at ICCROM are the exchange of experience and of know-how in the Mural Painting Course (3), where participants prepare murals using techniques specific to their own regions, and the sharing of expertise in order to undertake collection surveys or conservation projects on the PREMA (4) course.

This method also means recognizing the importance of communication and striving to improve it. With this in mind, a short course on communication skills which ICCROM has offered for 10 years now, has been specifically introduced into some of the teaching programs (Scientific Principles in Conservation Course, PREMA course).

Vive la différence

There is perhaps a larger issue in linking the question of multiculturalism to conservation training. In fact, in a field such as ours, tightly linked as it is with culture and traditions, it could be worthwhile to explore further how knowledge is transmitted in different societies.

In the occidental world, where the concept of conservation has been formalized, education is largely based on the accumulation of data: the more you acquire, the better you are prepared. In fact, the current focus of discussions on development of conservation training programs is how to dispense more information and to teach more skills, resulting in an increased duration of programs. Multidisciplinarity in the conservation field certainly does not help to correct such a trend.

Perhaps we should consider abandoning this infinite quest for information and concentrate on developing the abilities of participants to find and manage information, and to construct a mature and responsible attitude to face the conservation problems which they will confront. Training in a multicultural en-

vironment gives us the opportunity. It provides the impetus to reflect globally about conservation and heritage and to think differently on our approach to training and education. A beautifully rich mosaic and a challenging puzzle, too.

Acknowledgements

We are indebted to the ICCROM program coordinators, and especially to Gaël de Guichen, and the head of the ICCROM library for their collaboration.

Notes

1. Since 1986, ICCROM has collaborated with Intercultura, a non-profit intercultural exchange organization (part of the network of AFS International) to integrate intercultural activities and support into the PREMA program (see note 4).
2. PAT - International course on the Preservation of Earthen Architectural Heritage, co-organized with Craterre, Grenoble, in 1989, 1990 and 1992.
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Abstract

The MA in Conservation of Historic Objects (Archaeology) course at the University of Durham (UK), which developed from the previous Postgraduate Diploma in Archaeological Conservation, trains and educates students, over 2 years, as conservators of historic and archaeological objects. The skills of planning, organisation, management, implementation and communication are all required by conservators working in the present day conservation industry. The Durham course enables the students, through a series of projects - conserving whole site assemblages, environmental monitoring, storage, and disaster planning - to learn these skills. This enables the student, if required, to competently and confidently engage in large-scale passive conservation programs when they enter employment.

Keywords

Training, education, qualification, projects, curriculum, passive conservation, course

The Development of Managerial and Communications Skills in Conservation Trainees: The Durham Experience

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Introduction

The original Durham conservation course, developed in the mid-1970s by Janey Cronyn, and which gained an international reputation, was a three-year course leading to a Postgraduate Diploma in Archaeological Conservation. Since 1990 this course has been modified to a two-year course leading to an MA in Conservation of Historic Objects (Archaeology). This higher degree and modified course represents a very intensive training, for six students each year, in the conservation of a wide range of historic and archaeological objects.

Over the last twenty years the emphasis in conservation has changed from object treatment to a much wider variety of preservation strategies. These include conservation management and the storage and environment work often inappropriately titled 'passive conservation'. It is apparent that young conservators need to be as familiar with this approach to conservation as they are with interventive object treatments(1). Conservation training courses such as the recently revamped course at Durham are addressing this requirement by developing the pro-active planning, organisational, managerial and communication skills of their students. These skills are most appropriately taught through student project work, rather than traditional lecture or laboratory-based practical training.

Qualifications and Courses

It can be suggested that many conservation courses currently undervalue the level of education and training they provide. The Durham course has raised its qualification to an MA, since the students were reaching this higher academic standard, but only being awarded a Postgraduate Diploma. Margaret Holben Ellis commented at the ICOM-CC Working Group on Training, Interim Meeting (Museum of Mankind, London, April 1992) 'that MA students in conservation subjects at the Institute of Fine Arts, New York University required as many credits as a Ph.D'. We should surely not disadvantage conservators when it comes to future salary and seniority levels in museums, simply because we as a profession deem long training periods and modest qualifications 'a good thing'. This attitude harks back to conservation's origins as a craft discipline, with training and education through long apprenticeships. Though often effective training, apprenticeships contained little education, and were often 'rights of passage' for the apprentices, serving principally to re-enforce the status of the master. The conservation profession is nowadays as much an industry or business as it is a craft, and consequently efficient, focussed, modern training methods based upon understanding, i.e. education, should be employed, regardless of whether teaching in the craft or 'conservation studies' areas of the subject. If as professional trainers and educators we are to do more than simply replace one form of master with another, then we must continue to develop realistic education-based training and qualification standards, and the legacy of previous long apprenticeships of craft-based specialisms should not blind us to the currency of qualifications in the modern world.

Is present day conservation more akin to an 'industry' or 'business', with students coming to learn the business (2), rather than a craft (3)? Attention has previously been drawn to the fact that conservators increasingly move jobs, have a career structure, are responsible for whole collections, buildings and people, and are often gathered into large groups or departments which require some form of managerial structure and organisation (4). These aspects of organisation, scale and responsibility are more accurately described as an industry or business than

a craft. This should not imply any lessening of 'hands on' skills, or a reduction in the appreciation of the unique character of each object. It also depends on the area of conservation which is under discussion, with perhaps more job movement, management and organisation in object collections (archaeology, fine art, ethnographic, social history, industrial) in large museums (4), than in small workshops specialising in 'art' conservation.

How do you educate and train students for this perceived conservation industry/business where they will have to deal, through a succession of jobs, with a large volume of objects from a wide variety of cultures? Clearly you must initially recognise the impossibility of giving any student a full knowledge bank of all the materials and objects which 100 years of conservation experience and the crowded shelves of fact-crammed scientific textbooks represent. Some form of critical assessment of what are the key elements in the training of a modern practising objects conservator needs to be created. This has been attempted several times; most recently Kate Foley (5) defined these mental and physical capabilities from the point of view of an employer of one of the largest groups of conservators in Britain. She focussed particularly on the general mental skills and personal qualities which equipped conservators to acquire the relevant knowledge bases as they progress through their conservation career, as well as the physical skills of manual dexterity and the mental concepts for making ethical and judgmental decisions. This matches well with the problem-solving approach advocated by Nicholas Stanley Price (6).

In addition to the fundamental basis derived for any education course, there must be a realisation that every society has finite resources, and will decide through the limitation of these resources the value which it places on that form of education. The increased use of short-term contract employment in Great Britain during the 1980s was in part responsible for the reduction in the numbers of student internships available. It thus became more appropriate to train conservators using the present shorter form of the Durham course with the consequent raising of the course's intensity, and a subsequent pattern of early employment through a series of short term contracts before students gain full-time posts.

MA in Conservation of Historic Objects (Archaeology)

Though the Durham course can be defined in curricular terms, it is fundamentally based on the student achieving a set of definable competences. These have been described in generic terms (7) as; 'competence in the cognitive, directive, operational and attitudinal domain' of conserving historic and artistic works. In specific terms we develop the competence of the student to:

- i) Appraise, analyse and record the materials and decay processes of objects from historic and archaeological contexts.
- ii) Derive appropriate conservation treatment or storage regimes, designed to preserve the object.
- iii) Where appropriate to visually reveal the true nature and form of the object.

In the current course format students come to Durham for their initial year of academic training. Teaching is given in a wide range of formats; lectures, seminars, tutorials, visits and practicals covering: archaeology, early materials and technology, scientific analysis, decay and conservation of metals, ceramics, glass, stone, leather, wood and mixed media objects as well as field conservation, lab safety and organisation, and environmental monitoring and control. Other topics are only briefly covered since they are the province of specialist conservators, e.g. conservation of paper, plastics, textiles, wall paintings, works of art on canvas, ethnographic and geological materials. The practical work of the Durham course deals with recording, analysing, cleaning, conserving and, where appropriate, restoring a wide variety of archaeological and social history items. Students work on objects from Durham's Oriental Museum, Beamish Open Air Museum and the Archaeology Department's excavations. Following the exams at the end of the academic year, the summer is spent in the conservation laboratories in Durham further improving the students' practical skills. The whole of the second year is spent on an internship in a conservation laboratory in a

British museum or heritage agency, e.g. the National Museum of Wales, National Museums of Scotland. This gives the student a total of 15 months' continuous practical work and represents our emphasis for 'hands on' experience. A 10,000 word dissertation and a portfolio of conservation work are completed during the second year. Thus far all students who have completed the Diploma and MA courses, and who wished to stay in conservation, currently have jobs in the profession.

Project Work: Purpose

The conservators responsible for the extensive multi media collections which fill most museums and historic houses, clearly cannot ignore parts of the collections simply because they are not familiar with the materials involved or have not specialised in that area of conservation. It is essential to have developed coherent strategies for caring for and conserving the whole collection; recognising threats to the continued well-being of objects, prioritising them and gaining the resources for the necessary conservation and storage work. This will often involve organising specialists, e.g. conservators, for dealing with specific objects. Previously this work was often the province of the curator; however, as the process of caring for collections has become an intensely scientific one, and curators have become increasingly responsible for organising exhibitions and dealing with the public, the care of collections is often being passed to conservators.

To meet this changing and challenging role for conservators, the Durham course develops a pro-active and holistic approach to conservation and seeks to develop the planning, organisational, managerial, implementational and communication skills of its students. This fundamentally means giving the conservators the confidence to get out from behind their laboratory benches, critically analyse the problems facing the collections, devise and cost solutions, persuade people to give them the resources to tackle the problem, and then successfully implement the solution. This whole approach is asking a lot of a recent graduate who is just starting to train as a conservator. If, however, they understand that it is often the most effective way to keep an object intact or get an object preserved, and they are familiar and comfortable with this method of conservation, then they are much more likely to use these methods. Its incorporation into the training of the course re-enforces for the student the idea that this form of preservation can be as valuable and satisfying as any 'hands on' treatment. This avoids students retreating behind their conservation benches and white coats when they finally arrive in the workplace.

Project Work: Practise

It is difficult to effectively teach subjects such as planning, organisation, management and communications in a lecture, tutorial or seminar format. These skills are very personal ones, not pieces of knowledge which can be absorbed and regurgitated at the appropriate time, but rather a way of dealing with things which is effective and sensible. In the same way as one learns to clean and conserve an object as one works directly with it, so one learns to plan, organise and manage by actually doing it.

In the Durham course we have used the format of challenging the students, often as a group, with a series of projects which run throughout the first year, as the principal means of getting these ideas across. After initially outlining the task, the students are left to organise themselves to plan what they are going to do, seek and gain the resources to do it and then organise themselves to do it. The progress of the project is monitored by a member of staff.

Since Durham University is fundamentally a 'higher education institution', it is inappropriate to simply train students to perform a task; the process must be an educative one. Thus it is essential that the students critically analyse the project, so gaining an understanding of the process they are undertaking in deriving a solution to the project. At the end of the first year summer the students each give a seminar on one of the projects with which they have been particularly concerned. This not only develops their communications skills, and

incorporates a point at which the project is evaluated, but it holds up the project for peer review. The project is then written up as an item for the student's portfolio. This encourages them to not only argue for the course of action taken, but, as in every portfolio item, engage in critical appraisal of the process carried out.

Project 1: Excavation Finds

In order to make the students think about a collection as a whole, they are given all the small finds, principally iron and copper objects from a recent season's archaeological excavation. The students are informed that they alone are now the conservators for the site, and that they have to record, investigate, store and conserve all these finds. Since there is no prior selection, they have to X-ray all the ironwork, and consult with the excavation director selecting the objects for conservation, for complete or partial cleaning. This process familiarises them with the large volumes of often unidentifiable finds from archaeological excavations and enables them to see that the relevance of these objects is to the archaeological matrix from which they come, as they rarely have intrinsic aesthetic appeal or value. The students soon learn the reality of not spending an inordinate amount of time cleaning an unstratified find which has no archaeological relevance, when they still have the rest of the site assemblage to conserve. This concept of objects having a context is much clearer than if they were working on a single selected object. The responsibility of acting as the conservators to this site undoubtedly makes them take their training more seriously.

Work undertaken.

1990/1991/1992; Finds from Dryslwyn Castle Excavations, director Dr C. Caple.

Project 2: Environmental Monitoring

The students, in groups of two or three, are made responsible for monitoring a gallery or store in a local museum. They monitor using thermohygrographs which require the paper to be changed weekly, and check the thermohygrograph calibration using an electronic thermohygrometer. The discipline of planning and organising the changing of the thermohygrograph paper, particularly during the vacations, is an important challenge to the students to organise their own time and to work cooperatively. They are expected to acquire additional information, e.g. document the RH, temperature and light variations within the room and obtain data about the exterior weather conditions. Finally they draw this information together into a report. This contains graphs depicting temperature and RH information, appraisal of the nature of the collections and the construction of the room and building, explanation of the overall levels and fluctuations in temperature and RH and, finally, suggestions for future control (if necessary) of the environment. These reports form a valuable resource, provided free, for our local museums and art galleries who act as hosts for our monitoring work. This project is an excellent method of making the students think about what environmental data actually means to the future well-being of a specific collection and the work gives the students face-to-face contact with the curators of these various museums. This familiarises the students with the role of conservator, and makes them realise the importance of such work if colleagues are going to act upon their recommendations. There is often an interesting period of realisation when students perceive an environmental problem, but realise that air conditioning, or other high tech interventive control method is simply not financially possible for their host museum.

Work undertaken.

1990; Fulling Mill Museum, Attic and Basement Store
1991; Fulling Mill Museum, Display Gallery
1991; Oriental Museum, Long Store
1992; Fulling Mill Museum, Attic Store
early records 1984-1988

1992; Newcastle Museum of Antiquities
1992; Newcastle University, Hatton Gallery

Project 3: Storage Project

The students are confronted with an area of the collections which require re-storage, or objects which require specialised storage conditions or facilities. There is a considerable challenge for many students in the practicality of not only devising their own solution, but getting it costed, preparing a grant application, ordering materials, and then assembling the new storage system. It gives them real confidence to successfully get a grant and to see something they 'dreamed up' come to reality. The benefit derived from the experience of having to find product suppliers, use telephones, write letters and work out sales tax should not be underestimated. The final experience of having to 'roll up their shirt sleeves' and practically assemble the storage system they have devised can be a salutary one and is a very pertinent experience before the second year internship.

Work undertaken.

1990; Coin and Samian Collection: initial studies
1990; Classics Collection moved into Fulling Mill Museum
1991; Oswald Plique Samian Collection
1992; Dryslwyn Castle, Iron Hinges

Project 4: Disaster Plan

Preparation of disaster plans is currently being undertaken by almost all museums in Britain, and provides, towards the end of the year, an opportunity for the students to become familiar with a museum's collections and its buildings. The process of analysing the building, its daily activity and routines, and looking for potential disasters makes them highly aware of the constant threats that exist to collections. Research skills are developed as the students assemble lists of local facilities and suppliers of equipment for dealing with fire, floods, etc., and communications skills are enhanced as they involve the museum curator in the project process. The requirement to assemble a sensible, intelligible, formal disaster plan document reinforces the need for clarity of thought and common sense solutions. The production of the document demonstrates the need for skills in clarity of written and diagrammatic information.

Work undertaken.

1991; Fulling Mill Museum
1992; University of Durham Collections

Conclusions

The very act of doing a series of projects, develops in the student a sense of self-reliance. As in life, you do not find all the answers in the books on the library shelves. For any project you must first acquire information from a wide variety of sources; only then do you commence the planning, organisation and management of the project. This, clearly, mirrors conservation when defined as a business or industry where changing jobs and having new responsibilities requires that you acquire a new knowledge base before you start to make your decisions, plan, organise and manage.

These projects which have encouraged and developed self-reliance will, by that very process, also develop confidence. Students will also have gained confidence from completing the 'hands on' conservation of objects, but the completion of a storage or environmental monitoring project is something much larger and more complex. It has involved a greater range of decision-making and it makes the conservators of the future not simply accept doing things on the single object scale, but think about solving problems for whole collections.

In general, storage projects, disaster plans, environmental monitoring, and condition surveys, are under-researched and reported. They rarely appear in the

conservation journals and publications, though there are some notable exceptions. This work often appears less exciting to the students than analytical investigation or case studies of object conservation. The use of projects in the first year of the course opens up the possibilities to the student of doing this type of work for their dissertation. They may even recognise it as the area of conservation in which they might seek to develop a career.

The project process removes the students from the comfort of the university laboratory, and enables them to play the role of conservator to the outside world. Within the teaching department, they are constantly reminded of their role as students; this is reinforced with every lecture, practical or essay they do, they are always being taught. The project removes this mental 'arm lock' and, coupled with the whole of the second year out working in a laboratory, gives the Durham course students as great a degree of confidence in their own professional standing as it is possible to achieve within taught course limitations.

These projects have the combined effect of developing the students' overall independence, raising their confidence and increasing their planning, organisational, management, implementation and communication skills. It shows them that areas of conservation sometimes described as 'passive conservation' are anything but passive.

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Abstract

The growing need to teach and therefore to assess the "soft" attribute of professional attitude is commented upon, with reference to the development of the conservation profession and to external pressures, notably an initiative in Britain concerning standards in vocational education. The resulting implications are discussed, including the need to review the content of conservation programmes, to define objectives, to evaluate teaching and learning methodologies and to develop appropriate resources.

Keywords

Professional, attitude, assessment(+), training, education, vocational, standards(+), education

Professional Attitude: The Challenge to Education with Particular Reference to a Post-graduate Programme

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Introduction

A professional attitude is an illusive and possibly contentious attribute which practising conservators need to demonstrate. Its teaching is not easy and its assessment extremely problematic. This paper discusses the need to include attitude in programmes for professional conservators, and looks at some of the reasons why consideration of attitude and of assessment have become especially acute in Britain in recent years. We then outline how the teaching of attitude is effected in one particular post-graduate programme and detail the implications for teaching and assessment resources.

Education for Professionalism

Over the past twenty-five years conservation has been developing into a profession (1); it has followed the sequence of steps common to any evolving profession (2). Jarvis (1983) goes on to define professionalism as the combination of dedication to becoming a master and commitment to the occupational organisation. If we seek to educate professionals, we must develop not only the knowledge, understanding and skills of the discipline but also a professional attitude; not only cognitive and psychomotor aspects but also affective ones (3). As Jarvis shows (4), a professional attitude encompasses not only the knowledge of professionalism but also a commitment to it and a willingness to act professionally; not only the "can do" but also the "will do" (5). One way of showing the difference between cognitive activity and affective behaviour is to look at the associated verbs (6). Whereas knowledge and understanding can be described, as complexity increases, in terms of "state, identify, predict, analyse, summarise and evaluate", corresponding affective verbs describing behaviour would be "receive, answer, participate, relate and change". What is needed is not only a degree of self-awareness to distinguish between good and bad practice both in others and ourselves but also an emotive commitment.

Whilst for many years elements of attitude have been enshrined in the practice of conservation through Codes of Ethics, it is becoming more apparent that a professional conservator should have specific skills in these areas. This development was discussed at the Interim Meeting of the ICOM CC Working Group on Training held in the Netherlands in 1989 (7). It has been brought about for a number of reasons generated by the practice of conservation, including the need for better communication (8) and the increasing pressure for accountability. However, little has been said in particular about what we will refer to specifically as an "attitude of professionalism" to distinguish it from "knowledge of professionalism".

Although professionals are under an obligation to continue to learn throughout their career, there are two questions we ask. First, what role should education/training programmes take in the development of professional attitudes? It is now usual to argue that some level of professionalism must be included (9) and many programmes offer elements concerning "professional or business aspects". However, they appear to focus on the knowledge and understanding needed (the "can do") rather than the affective ("will do") aspects. The extent to which both the cognitive and the affective aspects should be covered still requires discussion (10). This decision as to what objectives to set in programmes concerning professional attitude would be more easily arrived at if our profession had means of licensing practitioners (11). But until we succeed in setting up comprehensive accreditation systems, we have to look to the education/training

programmes to ensure that at least the grounding of standards in such areas is ensured.

The second question concerns the extent to which professionalism *can* be covered by teaching programmes. One consideration is that of the amount of programme content. Programmes are already so full of matter that developing a new area will mean the loss, at least to some extent, of another area; the only alternative is a thorough overhaul of the curriculum (12). A second consideration is how far can structured programmes go in teaching professionalism; when are other means more appropriate? How far *can* structured programmes contribute to learning of attitude, the "will do" rather than the "can do" aspects of professionalism? A third consideration is the limitations of assessment within programmes; if objectives of professional attitude *are* set, then means for assessing the achievement of these objectives must be in place. Assessment of any aspect of education/training is not easy and assessment of "soft" aspects such as "attitude" is particularly difficult (13) but if we as educators are to maintain standards of professionalism in our qualifications, we must review our methods of assessment to check that they are appropriate and functioning.

External pressures for review of conservation education

Whilst some of the pressures for review, as shown above, come from the profession itself, there are also pressures which are wholly external. One of these in Britain today which gives considerable cause for debate relates to the Government's directive that all education should be tailored more specifically to work. This directive now extends to the development of Standards in Education/Training in the heritage sector by the Museums Training Institute (MTI) (14). There are two core characteristics of this initiative. The first is that the Standards being derived are described in terms of outcome, of competency which is related to the practice of an occupation carried out in a real work situation. The second is that the bulk of assessment is to take place as a candidate demonstrates competency whilst at work. The Standards and assessment of such competency in conservation are in the process of being devised and they do include the demonstration of some aspects of professionalism (15). It is difficult to determine really how far these cover the affective factors of commitment and willingness. Since the MTI assessment of competency can allow for experience or qualifications obtained prior to the work being judged to be taken into account, qualifications offered in "professional" conservation which should include this soft element of "attitude", will be appropriate here.

In Britain as elsewhere, there is a second growing external pressure on tertiary education, that of the world recession. This means that, even for education, fewer and fewer resources whether private or public are available. Other external pressures on assessment include the demand being made by the Higher Education Funding Council. Universities are being asked to produce more detailed evidence than ever before of quality assurance including assessment. Furthermore, students are becoming subject to a more competitive study and work ethos, to a need for more individual guidance and, rightly, to an increased emphasis on freedom of information. They are asking for more feedback. This changing balance of needs which the authors have observed requires to be examined by teaching institutions which then need to ensure that their teaching and assessment procedures are appropriate. This requirement should be met without loss of independence and quality, the hallmarks of higher education.

The teaching of professional attitude; a case example

In order to demonstrate the complexity of the problem of teaching professional attitude, we now discuss our work with the Diploma in Textile Conservation, a discussion which will also indicate particular aspects on which to focus debate.

The Textile Conservation Centre (TCC), near London, offers to graduates a three-year programme leading to the University of London's Courtauld Institute of Art Diploma in Textile Conservation. During nine academic terms students study and work on historic textiles normally under the guidance of a tutor but on occasion with a member of staff from our Conservation Services

division (16). It is interesting to note that, although the teaching of professional attitude has been implicit since the course was established in 1976, this key objective has only been made apparent since 1990. The overriding aim of the 1992/3 programme as stated in all programme documents is:

to enable students to acquire the necessary knowledge, skills and attitudes to practise general textile conservation within the professional framework.

Thus we do see the Diploma as teaching and assessing professionalism which includes attitude as well as knowledge and skills.

Teaching of the professional *knowledge and skills* is done as in most programmes both formally and informally. Thus in all three years we have lectures/seminars/assignments related to ethics and to the framework in which conservation is practised. We start teaching perhaps one of the most crucial tools for the professional, communication skills from the first year. Health and safety matters including responsibility to others are also introduced in the first year. In the final year we offer classes introducing business management and life skills such as writing c.v.s and interview techniques and, more informally, on estimating and project management. Being graduates, students are also expected to learn a considerable degree of professional practice through informal means. This includes owner/client liaison which from the first year is encouraged through formal group discussion of proposals for treatment through to viva/oral examinations in their final year.

It is much more difficult to say how professional *attitudes* are taught and even more difficult to say how they are learned. For this reason, programme objectives in this area are soft but overall we try to encourage an attitude whereby value is placed on professionalism, and that there is a commitment and willingness to act professionally. Like most other professional programmes one can demonstrate in formal sessions the meaning of and the need for "will do" but it is through "socialisation" that much of the learning comes (17). It is through example, role models and experience that teaching is implemented. At the TCC we are extremely lucky to have a Service division working alongside the students thereby broadening the pool for socialisation to include practitioners as well as teachers. Students also benefit from a shared tea-room, a perhaps underrated learning environment. Students are encouraged to undertake vacation work in other professional workrooms and to join the professional societies. We also have a constant stream of overseas interns and visiting scholars working at the TCC and widening students' contacts. There are many other examples of formal and informal learning situations such as open seminars for ex-students and the demonstration of staff commitment to publication, membership of professional committees/workshops and continuing self-development, but the above may suffice to outline the range.

We believe that a professional attitude is based on two key attributes; namely self-awareness and a sense of responsibility. To function as a professional, a conservator must have confidence in his/her abilities and knowledge; they must also be both constructively self-critical of these attributes and able to motivate themselves to improve where they see problems. They must take responsibility for their own actions and extend this to group responsibility. Thus we attempt to develop these attributes in students. Our overriding aim is to seek to ensure that our students can and will be able to work within the professional framework without eliminating creative and open-ended thinkers or producing incurious conformists. Such an aim is a crucial aspect of education, as against training, and we would argue that education is what conservators need, not just training.

Considerations arising from inclusion of professional attitude in programmes

One of the major considerations for programmes which have objectives concerning professional attitude is its assessment. Very little even on more general assessment in conservation education has been published (18) to date even though it is widely referred to when programmes are described (19). Some guidance can however, be found in the education literature. Foremost, it should be noted

that assessment is a multi-purpose process. Rowntree (20) identifies six main reasons for it; maintenance of standards, motivation of students, feedback to both students and staff, preparation for life, and selection.

There are numerous methods of assessment to meet various needs but it cannot be taken for granted that an existing method is appropriate. Thus, whilst University education is founded on the creation of an ability to distinguish between good and bad knowledge, the ability to distinguish between good and bad practices and to value and seek to enact the former is not enshrined *de facto*. Educators must look for or develop methods of teaching and assessment which can accommodate this soft attribute of attitude. Although the assessment of attitude is a commonplace in some subjects such as medicine and social work, it is fraught with danger. This is particularly so when assessment is being used for reporting to others rather than for feedback to a student; it can easily be coloured by our perceptions and the nature and length of period of contact between ourselves and the student (21). Thus we must be absolutely clear what we are assessing and how we are doing it. Lastly morality must be considered; any touch of indoctrination is to be abhorred.

One method of deriving assessment objectives and methods is through the development of detailed competences (22). From these, performance indicators are derived which can be used to assess achievement of the competences. This method has been used in the MTI initiative described earlier and has produced some performance indicators covering aspects of professional behaviour (23). However, it is extremely difficult to see yet how assessment of these competences by observation and questioning can really cover not only the considerable underlying knowledge and understanding needed but also the commitment, valuing, participation and other aspects of attitude expected from a professional. It is reported by Seguel that also in Chile "attitudinal" competences for conservation have been derived. Unfortunately, the translation of the document in question does not cover them in detail (24).

Another potent consideration of teaching and assessment at the moment is the "cost", in terms of time, space and staff expertise. Not only must both staff and student time be set aside, suitable space must be found for both one-to-one tutorials and for group sessions. This demands careful planning and attention to submission and tutorial dates. Where individual staff teaching rooms are not available, planning and timetabling become more acute, organisation which must withstand problems of illness or late completion.

Consideration of staff expertise is especially important. To feedback to students comments concerning their progress towards affective objectives in a way in which the student can use them requires considerable skill overlying an appropriate personality. A high development of these particular skills and traits of personality are not necessary for someone entering the conservation profession but they are vital for advanced level assessment. Thus conservators and others who take up teaching should be given support to help develop these attributes; commitment to teaching alone is not enough. One support method we have used at the TCC was to arrange group sessions with an educationalist for all teaching staff. One of these sessions on *Behavioural Analysis* was found to help us understand more clearly the way in which we relate to students, an understanding vital to the assessment of "attitude" as well as to feedback sessions. Skill and time are also needed if written comments are to be disclosed to students. It is extremely easy to destroy or inhibit progress with a poorly considered phrase; to write an accurate as well as helpful report requires considerable time and perceptiveness. If written comment conveying assessment of attitude to another person is to be used for selection, maintaining standards or any other process, similar care is crucial. We must also as teachers be aware of our limitations and to know when the student needs skills other than our own to deal with difficult life problems.

Conclusion

The nature and extent of the learning of professional attitude in conservation programmes requires further discussion. The methods by which this can be

taught need to be examined both in relation to the ideal and the practical. Even more illusive are the means to assess professional attitude; morality as well as methods must be aired. The more we are able to share not just ideals but also realities and experiences, the more productive such discussion will be.

Teaching and assessment of professionalism require considerable resources which include investment in staff teaching skills both at the initial stage of a conservation teaching career and in continuing development. Investment in resources is ongoing; curriculum content and assessment procedures need continuing review as external pressures change. The implications of this cost of education (not just training) must be considered in the light of the political as well as the financial environment.

Until we can achieve a professional accreditation scheme, considerable responsibility in maintaining standards of attitude rests on programmes which purport to provide practitioners ready to embark on a career in conservation. Both students and employers must be clear on what particular programmes can and do offer. However, surely practising professionals/ employers too must take responsibility for developing professionalism in their new recruits; it cannot be left to structured programmes alone.

Assessment and teaching is not all that educators in higher education establishments should be doing; we should also be developing knowledge and maintaining quality in endeavour. Whilst we continue to develop teaching and assessment techniques and to maximise efficiency and effectiveness, we must of course maintain course enjoyment; without this latter element, all else palls.

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Abstract

This report is a historical account of the conservation and restoration training that has developed in Cuba since 1960 to meet the needs of museums. It gives examples of the programmes taught in the two last decades by the National Centre of Conservation, Restoration and Museology, and describes a plan to create a Master's degree course for university graduates in the arts and sciences. It emphasizes the close connection between research and teaching and the employment possibilities for trainees under the state planning system.

Keywords

Research program, tropical climate, laboratory, Master's degree, Cuba

Conservation and Restoration Training in Cuba—Present and Future

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Antecedents

In Cuba, training in conservation and restoration began to develop in the 1960s in response to needs created by the growth in the national system of museums (see Fig. 1). In 1958 there were ten museums in Cuba. Since 1960 they have been reorganised and more museums were created in palaces and historic residences of the 18th to 20th centuries, so that by 1990 the number of museums had increased to 256.

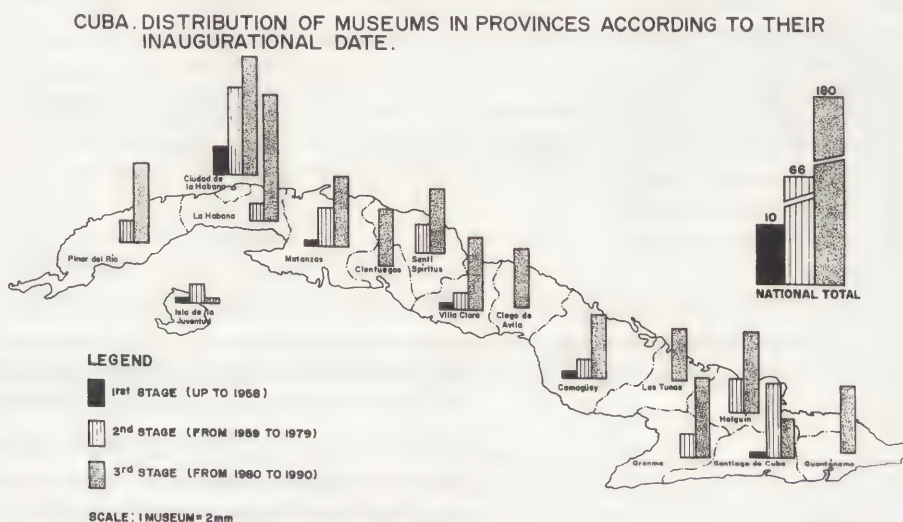


FIG. 1

The volume of objects that constituted the heritage of the nation required the urgent training of technicians in restoration. At first, only the National Museum of Fine Arts, situated in Havana, had a few artists who worked as conservators in a poorly equipped workshop. Added to this small group there are now graduates from the new schools of technology in fine arts, and many of them have travelled abroad in order to specialise (e.g. the former Czechoslovakia, Russia, Germany, Poland, Mexico, Italy, Spain and France), assimilating the experience of various international schools, and enriching the points of view and approaches to work in Cuba.

While this first generation of technicians possess significant technical knowledge, there are however gaps in their theoretical and scientific experience.

At the same time, the National Museum of Fine Arts receives foreign specialists who give lectures and training for a short duration in workshops which have been enlarged and provided with essential technical equipment. It also receives trained employees from other provinces who have created small conservation workshops. Other national institutions such as libraries and archives have created conservation departments specialising in paper and bookbinding. Most of these are located mainly in Havana (see Fig 2, Table 1).

In 1979 the Institute of Museology was founded, affiliated to the Ministry of Culture, in order to train museologists to cover the needs of the many newly-founded museums. The two-year programme included the subject of conservation of cultural artifacts.

The Present Situation

In 1982 the National Centre of Conservation, Restoration and Museology (NCCRM) was founded with aid from UNESCO. This institution of the Min-

Table 1. Areas of conservation specialization in Cuban institutions.

Institution	Provinces	Specialities							
		Paper	Tex- tile	Metal	Stone	Easel Paint	Mural Paint	Wood	Lab
NCCRM	Havana city	x	x	x	x	x	x	x	x
National Museum Fine Arts	Havana city	x			x	x			x
Museum of the City	Havana city	x		x	x	x		x	
Museum of the Revolution	Havana city			x	x			x	
Municipal Museum of Guanabacoa	Havana city			x		x			
Decorative Arts Museum	Havana city		x	x	x				
National Archive	Havana city	x							x
Institute of the History of Cuba	Havana city	x							x
National Library Jose Marti	Havana city	x							
Institute of Literature	Havana city	x							
Provincial Museum P. del Rio	Pinar del Rio			x	x				
Provincial Museum Matanzas	Matanzas			x	x			x	
Gener y del Monte Library	Matanzas	x							
Provincial Museum V. Clara	Villa Clara			x	x		x		
Decorative Arts Museum	Villa Clara			x	x			x	
Provincial Museum Cienfuegos	Cienfuegos		x	x	x		x		
Provincial Museum S. Spiritus	Sancti Spiritu			x	x	x	x		
Provincial Centre of Conserv. Restoration, Trinidad	Sancti Spiritu		x	x	x	x	x	x	
Provincial Museum Camagüey	Camagüey			x	x	x	x		
Provincial Museum Holguin	Holguin			x	x				
Provincial Museum S. Cuba	Santiago			x	x	x	x		
Total	21	8	4	15	15	8	7	5	4

istry of Culture has a technical and professional Cuban staff trained in the different specialties of the cultural heritage.

Since 1986 the NCCRM has developed a research programme in the preservation of the cultural heritage under tropical conditions, with special reference to the introduction of natural substances and local materials. To this end, laboratories have been set up to carry out technical analyses of organic and inorganic materials, giving considerable emphasis to specifically Cuban conservation problems.

In 1987, the department of conservation of artifacts was created, with a series of workshops emphasising the interdisciplinary relationship of science, art and technology.

This is a time of great teaching activity in the preservation of cultural heritage. A system of technical and professional training is in place. Seminars are offered at the NCCRM headquarters and in other provinces, in order to make museum



FIG. 2

staff aware of environmental risks, especially in a country with high salt levels due to the proximity of the sea.

In 1989, training began in easel and mural painting, textiles, paper, sculptures, metals and wood restoration. This was aimed at restorers from other provinces with an artistic background, and consisted of monthly meetings throughout one year. The training programme includes 65 hours dedicated to basic sciences, organic, and inorganic chemistry and microbiology. It covers applications to the most frequently used materials in heritage objects and their deterioration, and the use of substances and chemical products in restoration. Subject coverage includes simple laboratory analysis and the interpretation of more complex tests.

As long as a proper scientific, material and technical basis has been taught and the results of research on specific problems of preservation in tropical conditions have been presented, conservation training will acquire a national autonomy and will depend less on training from abroad. Only in some specialties, for example, the conservation and restoration of antique furniture, has a foreign specialist (from England) been employed to train Cuban personnel.

However, access to this Cuban system of professional training is still limited to graduates of art schools. Since specialists with scientific backgrounds working in heritage preservation in Cuba is an innovation, the various laboratories in the NCCRM allow microbiologists, biochemists and engineers without technical or artistic knowledge to take part in training projects.

The Future

Cuba has the experience plus the technical and material facilities for a university graduate to be able to specialise in conservation and restoration of artifacts, and could therefore create a Master's degree at the High Institute of Art and the NCCRM.

The dichotomy between those with arts and those with science backgrounds is overcome with a study programme consisting of three groups: a history-artistic group, under specialists from the High Institute of Art; a scientific group, under the NCCRM laboratory staff; and a technical group under the conservator-restorers of the Centre, depending on the speciality chosen. The preliminary program includes specialties in easel and mural painting, paper and sculpture, and has a 900-hour duration.

The entry requirements are different for the art history and science graduates because they have to pass a practical aptitude exam in fine arts and general culture. Those graduates in history of art, drawing, sculpture and painting are given credits in these subjects, whilst the science graduates can receive credits in applied science and conservation.

Programme

Historic-artistic subjects:

- General history of art
- History of Cuban art
- Painting
- Drawing
- Sculpture

Scientific subjects:

- Applied sciences-conservation I-II
- Materials of cultural heritage
- Preventive conservation

Technical subjects:

- Museology
- Technical graphics I-II
- Documentation of process
- Workshops

Employment Possibilities for Conservator-Restorers

The specialty of conservation and restoration of cultural artifacts is regulated by a specific law of the Cuban Ministry of Culture. It includes four categories:

- * The conservator-restorer "c", graduated from a technical school of fine arts with training in restoration.
- * The conservator-restorer "b", also graduated from a technical school, with training in restoration, and certificates of experience.
- * The conservator-restorer "a", graduated from university with specialist studies.
- * The high-level specialist, trained abroad (until now) with years of experience and concrete results.

The salary in each category depends on the degree of specialisation. The job security of the conservator-restorer is supported by a planning study of the future needs and the technical qualifications for each national institution that has workshops and laboratories. In addition to the course entrance requirements, there must be a request from the institute which employs the technician or a certificate that guarantees that every qualified person follows ethical and professional principles and is entitled to receive refresher courses to keep them "up-to-date".

Conclusions

- 1) Conservation and restoration training should be supported by an institution with a scientific and material basis that allows for the development of integrated programmes.
- 2) In developing countries, teaching should not be separated from research into alternative solutions to address the problems of scarce material resources.
- 3) The conservator-restorer's training should develop on two levels: the technical-professional and the graduate in art and science with a master's degree.
- 4) Entry into conservation training should be planned according to institutional needs and the availability of resources, thus guaranteeing employment for graduates and opportunities for systematic refresher courses.

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Abstract

A Code of Practice for Conservation Education and Training is proposed for all conservation teachers involved in the education of conservators at any level. It is aimed at assisting teachers in developing, promoting and evaluating their courses, with guidelines as to their responsibility to students, colleagues and the conservation profession.

Keywords

Code of Practice, conservation, education, training, teacher, course

Code of Practice for Conservation Education and Training

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Preamble

The Code of Practice for Conservation Education and Training provides guidelines as to the minimum requirements for those involved in the education and training of conservators at any level and in any field of conservation. It is equally applicable to teachers in universities, cultural institutions and conservation centres.

The Code of Practice is not intended as a set of standards by which to judge conservation training courses, but rather to assist teachers in evaluating themselves, their performance and the courses they teach. It is also to assist them in developing, stating and implementing a comprehensive policy for the recruitment, education and training and support of conservation students.

The idea for this document was initiated by the Code of Ethics for Museum Training which has recently been developed by the ICOM International Committee for Training of Personnel. It also takes account of *The Conservator - Restorer: A Definition of the Profession*, prepared by the ICOM Committee for Conservation Working Group for Training in Conservation and Restoration, and adopted by ICOM. In addition, information has been collected from other relevant publications and sources in an attempt to provide a global view of conservation education and training. Comments and input from the conservation education and training profession are welcome.

Definitions*Conservation/Restoration*

Conservation (or restoration in some countries) is defined in *The Conservator - Restorer: A Definition of the Profession*, as 'action taken to make a deteriorated or damaged artefact understandable with minimal sacrifice of aesthetic and historic integrity'. It refers to conservators of works of art, artefacts and information resources, and it is also applicable to conservation architects, educators, scientists and others involved in the conservation field.

Education and Training

It is important to distinguish between education and training, both of which should be included in any conservation course.

Conservation Education should offer a student the necessary intellectual skills to understand an object's history, technology and aesthetic importance, to grasp the science of materials, deterioration processes and preservation, and most importantly to develop a critical and analytical approach to the ethics of conservation (based on the above Definition of the Profession, or on the Codes of Ethics and Guidelines for Conservation Practice developed in a number of countries), and to understand debates about the nature of culture. It should, and

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sometimes must, include a number of other academic skills such as communication, management and the use of information technology.

Conservation Training on the other hand, provides the opportunity to put into practice in a studio or laboratory, the classroom-acquired skills. It is here that manual dexterity, observational ability and less tangible attributes such as common sense are developed and tested. In conservation these skills are essential, and in addition to laboratory work need to be developed through opportunities for work experience and internships.

Conservation Training Courses

Conservation training courses:

- are those instructional or education and training activities designed to advance the knowledge and understanding of conservation and its role in the cultural heritage field and in society;
- can be as short as one-day workshops/seminars, through several weeks/months duration, to 3-5 years for courses offered by institutions of higher education;
- can either provide a basic introduction and understanding of conservation to related disciplines, prepare persons to enter the conservation profession or provide mid-career development;
- can be offered by an institution of higher education (University, College), international or national professional organisation, a museum/gallery/library/archive, or the private conservation sector.

Teachers

The term "teachers" is used to cover all persons who educate and train conservators through any form of conservation course discussed above. Teachers may or may not have formal qualifications and experience in teaching, but must be qualified and experienced in the relevant conservation discipline. They should demonstrate a willingness to become involved in the development of teaching skills, their own included, and course planning and development as appropriate.

Students

Students include all persons receiving any form of conservation education and training through an academic program or work enhancement/skill proficiency development program. They may be employed in the cultural heritage field as conservators, or in related professions; they may be just starting a professional career in conservation or developing their skills at mid-career; they may be museum guides or volunteers.

No person for reasons of age, race, gender, religion, national and cultural origin, marital status or physical disability shall be denied access to or participation in conservation education and training courses.

Institution

The teaching institution shall be that body, being an institution of higher education; museum/gallery/library/archive or other cultural institution; national or international professional organisation; or private conservation practice which offers conservation courses, at whatever level.

The Training Institution

Each training institution should have an agreed mission statement or aims, reviewed every five years, which reflect commitment to education, training and research. In addition it should:

- provide adequate resources for teaching and research e.g., classrooms, libraries, computer facilities, laboratories;
- provide overall administrative and financial support and service to conservation training courses;
- provide excellence in teaching and provide staff the opportunity to develop their teaching skills;

- promote and provide opportunities for research emphasising the fact that a good training course requires research input;
- provide procedures for the review and evaluation of new and existing courses to ensure that they are coherent, properly organised and provide students with learning experiences that meet the course aims and objects;
- ensure the involvement of students and professional groups in the development and review of courses;
- provide appropriate funding and staff : student ratios to enable students to be trained to a level of competency in theory and practice so that they are adequately prepared to enter the conservation profession;
- ensure the highest standards of training, at all levels, to meet the needs of the conservation profession.

The Training Program

Basic Curriculum

The basic curriculum for a conservation training course should include the following, taking into account the wide range of specialised fields of conservation which can be taught and the special needs of different countries. (These may include for example: paintings, art works on paper, library and archive materials, the range of historical, archaeological and ethnographic objects, furniture, outdoor sculpture etc.)

- Histories of art and civilisations
- Fine art/anthropology/archaeology/material culture
- Technology and materials science
- Conservation history and ethics
- Conservation theory and practice
- Preventive conservation
- Chemistry, biology and physics of deterioration processes and of conservation methods
- Conservation management and private practice
- Conservation and museology/librarianship/archaeology
- Conservation internship

Levels of Training

There are four levels of conservation training:

- Introductory course
- Career entry
- Mid-career
- Specialised

Depending on the level of the course and other special requirements, they will include some or all of the above subjects.

Introductory courses are provided for persons requiring an introduction to the conservation profession, such as curators, art historians, librarians and archivists. They should not be used for persons intending to become conservators if this is the only form of training received.

Career entry courses are to train persons to enter the conservation profession, and they will invariably enable the student to specialise in a particular field of conservation such as paintings, paper, archaeological objects, furniture etc. This specialisation is essential as conservators are employed in their field of specialisation. Such courses are normally offered by institutions of higher education.

Mid-career courses are provided to enable practising conservators the opportunity for continuous education and training. This regular updating of knowledge and skills is essential if conservators are not only to keep up with the developments in their field but also to do the best for the objects they conserve. Such courses may include current conservation processes, materials and analytical techniques.

Specialised courses are usually sharply focused on a technique or process in a specialised field of conservation.

Conservation Internship

It is recognised that an internship of at least twelve months duration is an essential component of any career entry course. Where this is not possible the course should provide adequate opportunity for work experience during the course.

Graduate Student

The quality and skills looked for in a student graduating from a conservation training course will depend to some extent on the level and duration of the course, but for a career-entry level course, graduates would be expected to have:

- a sound knowledge base
- the capacity to assess materials, situations and published information
- the ability to solve problems, make decisions and set priorities
- good communication skills
- research skills, i.e. the ability to use the literature and data bases, and to test solutions to problems
- an understanding of the need for and meaning of ethics
- a command of recording techniques
- practical skills and the ability to use the senses of vision, smell, touch and sound
- the ability to accept and provide constructive criticism
- the ability to work in a team
- basic management skills
- an awareness of the importance of the inter-relationship of cultural diversity, ethnocentrism and the construction of histories
- an awareness of the role of conservation in the cultural heritage field

Admission Requirements

Admission to a conservation training program should be based on the concepts of fairness, honesty and equal opportunity. All prerequisites for entry to the course should be clearly stated in the course information literature and made readily available to prospective students.

Financial Requirements

Any financial costs to students should be clearly stated in the course information literature.

Course Description

Course organisers will encourage high quality courses and subjects by:

- ensuring that each course and subject has clear aims and objectives which are available to students to help guide their course and subject choice;
- biennial course development and review discussions, including examination of failure and attrition rates, workload and relevance of the course to students' life and career goals, to ascertain whether the courses and subjects offered are challenging and stimulating learning experiences and are fulfilling the educational objectives and needs of students and, where appropriate, of employers.

Assessment Methods

Details of the assessment levels and standards will be provided, as will the types of assessment (e.g. essays, exams, tutorials) and the methods of evaluating them.

Evaluation should be fair, just and without prejudice and should provide the opportunity for feedback on the students' level of attainment and progress.

Qualifications

The course information literature will provide details of the qualification (certificate, diploma, degree), and the levels of attainment, if relevant, to be expected on successful completion of the course.

At the successful completion of a course each participant will receive, where appropriate, a document stating the level and category of training received and

the standard attained. This document will be signed by the administrative authority of the institution.

Where relevant, institutions will provide information on the levels of recognition (whether locally, nationally or internationally) which the course receives, and the professional implications of this information.

Where no qualification is offered for a training course, great care must be used in providing 'certificates of attendance' for participants, as they can be misused. If offered, and they are often required by participants' employers, the certificate should indicate the content and level of the course, any form of assessment carried out, and whether the participant attended all sessions.

Teaching Staff

The institution will appoint teaching staff who have the necessary skills, knowledge, experience and qualifications to provide the described training course. It is imperative that the teachers be in a relevant field of conservation specialisation, and desirable that they also have training/experience as educators.

Teachers also need to provide a role model for students of a commitment to scholarly values, to life-long learning, to professional and personal growth through critical reflection and self-evaluation, to accountability for one's own professional activities and a responsible and ethical practice of the conservation profession.

Students expect and value a teacher's competence in their subject areas, effective communication of their knowledge and experience, interest and enthusiasm for their subject, concern and respect for students as persons, and a commitment to facilitate learning for each individual student.

Personal Conduct

Teachers will act in a responsible manner, both legally and ethically, in all matters relating to the operation of the conservation training course. They should address with equity the different social and cultural needs of the students and shall maintain an unbiased attitude towards individual customs and traditions provided they do not infringe upon the rights of other teachers or students.

Teachers will continually update their knowledge and skills by consulting relevant literature, attending conferences and workshops and through professional development opportunities relating to in-service education and training.

Personal Interests

Teachers will not derive personal benefit from involvement in a training course apart from the recognised monetary and professional gains expected of such an activity.

Intellectual Freedom

The teacher and student must be free and in fact be encouraged to pursue intellectual inquiry without undue restriction, and to state or publish material considered relevant to the conservation profession, provided that such activities do not infringe on the same rights of others.

Research

Research and scholarly activity provide a sound basis for good teaching, therefore teachers should be encouraged and supported in this. The results of such activities should be freely disseminated to colleagues, students and the conservation profession.

Teacher Responsibility to Students

Commitment to Good Teaching

A commitment to good teaching will improve the quality of student learning. It moves students away from the superficial reproducing approach to studying, towards a deeper approach involving a search for understanding - through the

introduction of new teaching, learning and assessment methods. The following strategies will assist in this regard:

- encouraging independent learning
- supporting personal development
- presenting problems (problem-based learning in addition to problem-solving)
- encouraging reflection
- using independent group work
- learning by doing (a major component of conservation studies)
- setting projects
- establishing procedures for regular feedback from and to students on all matters affecting them and their study

Uphold Professional Standards

Professional conservators abide by and promote a code of ethics and the highest standards of conservation practice. The same is required in the education and training of conservation students.

Teachers should not use their positions to promote misinformation, prejudices or personal beliefs. Intellectual integrity in the presentation of information is the duty of every teacher.

Fair and Equal Treatment

Teachers will provide fair and equal treatment to all aspects of a conservation training course as regards content, fields of specialisation, course publicity and student selection. They shall also provide opportunities and support for the intellectual and emotional growth of students encouraging free inquiry in conservation practices.

Student assessment will be without prejudice, and teachers should recognise the diverse needs, backgrounds (including language, religion and culture) and capabilities of individual students, and ensure that assessment accurately reflects the individual's level of achievement.

Confidentiality

Teachers shall treat as confidential all information of a private or personal nature through contact with students. Information regarding student grades and assessments will be kept secure and treated with equal confidence except when authorised for release by the institution or the student.

Student Involvement

To ensure good communication and co-operation between staff and students it is necessary to:

- involve students, or their elected representatives, in course activities and course planning and review procedures;
- organise regular student/staff meetings with agendas and minutes;
- provide induction procedures and information for new students;
- ensure that time is available for the individual supervision and/or counselling of students.

Teachers' Responsibility to Colleagues

Professional Relationships

Conservation training programs/courses will strive to co-operate with each other and not compete for prospective students beyond the statements of factual information contained in the course literature. Such information will be made available to all potential students and other training courses.

Professional Co-operation

Teachers have the responsibility, where time and resources permit, to respond to requests for advice and assistance from the conservation profession, teachers

or students in other training courses, and the general public. Teachers should also develop skills in communicating the significance of their work to representatives of the media.

Professional service

Teachers have the same obligations as other conservation professionals to participate in the activities of the profession. In addition, teachers should attend meetings, workshops and conferences and, where appropriate, be involved in the organisation of such activities.

As time and resources permit, the teacher will promote conservation awareness to the general public through public presentations and lectures.

The teacher will exercise discretion in distinguishing between acts and actions executed, or statements made as an individual, and those carried out or made as a representative of the conservation education and training profession.

Post-Training Assistance

As the objective of all training courses is to advance the conservation knowledge and skills of a person, this should lead to better career opportunities. It will be the responsibility of the training course to aid and assist the graduates from courses in realising their potential through either additional training, internships, gainful employment, employment promotion or increased status.

Teachers are expected to assist students through circulation of job advertisements, in preparing for a job application and interview, or through letters of reference.

Responses to reference requests should be based on an objective evaluation of the student's performance. Subjective observations or personal comments which may well be relevant for the reference must be stated in a manner to clearly identify the source. It should be noted that in some countries freedom of information will enable the student access to all references, and references in confidence may not be acceptable to the potential employer.

Abstract

Most of the art conservation Ph.D. programs worldwide are either very recent or still in the planning stages. In other professional fields, Ph.D. programs are widely recognized as the primary vehicle for providing training in advanced research methodology and for producing university-level educators. Conservation is not appreciably different from other applied technical fields, such as agriculture or psychology, which have Ph.D. programs in addition to a body of practical techniques. Ph.D. programs train conservation professionals to contribute to the development and assessment of new materials and techniques in conservation, and to address art historical problems with an interdisciplinary approach that includes a technical component.

Keywords

Conservation education, dissertations, Ph.D., training

The Role of a Ph.D. Degree in the Education of a Conservator

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Introduction

Ph.D. programs specifically designed for conservators are available in at least four institutions. The first program was established many years ago at the University of London, which awards a research degree leading to a Ph.D. in conservation [1]. The University of Delaware initiated a Ph.D. in Art Conservation Research in 1990. It includes coursework in science and art history, foreign language training, and research culminating in a dissertation [2, 3]. The University of Canberra offers a Ph.D. in conservation while Göteborg University is in the process of beginning a Ph.D. program in conservation [4]. All of these programs are principally intended for those with a master's degree in conservation and/or practical experience as a conservator. In a related program at Johns Hopkins University, students in the Materials Science and Engineering Ph.D. program can write a dissertation based on research and studies of importance to conservation [5]. This program is primarily intended for materials scientists, although conservators may also apply if they are willing to remedy coursework deficiencies in materials science. Several other universities around the world have begun discussion and efforts towards establishing Ph.D. programs in art and architectural conservation research.

A few conservators have in the past pursued a Ph.D. degree in a related field such as art history, history of technology, or materials science. However, the existence of a variety of Ph.D. programs specifically designed for conservators is a new phenomenon that will soon result in a sizable population of conservators with doctoral degrees. With these newly-expanding Ph.D. options appearing internationally, it is worthwhile considering the role of the Ph.D. degree, by definition a research degree, in a field that is based on the practical application of hands-on techniques. I first review the general purposes served by Ph.D. programs in other fields, and focus specifically on roles that such programs might serve for the conservation field in particular. I then discuss issues concerning the research qualifications of Ph.D. conservators, and relate them to parallel issues that were raised when materials science was emerging as a new field.

General Purposes of Ph.D Programs

Undergraduate programs are usually intended to provide a broad educational background in addition to substantial knowledge in at least one major area. Master's degree programs tend to focus on a particular specialty, but within that specialty a broad understanding of the field is usually a goal. In contrast, Ph.D. programs provide a student with the opportunity to gain more detailed, specialized knowledge within one's chosen field. If not already done at the undergraduate or Master's level, Ph.D. programs often involve language training as well, so that a wider range of literature will be accessible to the student.

The backbone of any Ph.D. program is successful completion of a dissertation, which is intended to comprise original research on a topic of significance to one's field. By going through the steps of designing, implementing, and reporting this work in written form for review and critique by others in the field, the doctoral student receives basic training in all aspects of research methodology. After completing a dissertation, the graduate should have the ability to continue contributing to new knowledge throughout his or her lifetime, using the skills acquired during the doctoral work.

Exceptional persons with a high degree of motivation have attained the same research and writing skills on their own, without the help of a doctoral program. However, self-training without benefit of the support of an academic program

specifically designed to impart these skills in an established and efficient manner is difficult for many people. Thus it is no accident that in many fields the vast majority of the peer-reviewed and other published literature is produced by those holding a Ph.D.

In many fields, a Ph.D. degree is also considered helpful for those who will be educating the future professionals in the field. Thus most university departments employ professors with Ph.D.s for both undergraduate and graduate teaching. The Ph.D. degree is seen as useful in this context because it indicates mastery of a wide range of material within the field as a whole, as well as the ability to focus on narrow subsets of knowledge when necessary, providing the flexibility often required of university-level teaching.

It is also generally considered important that students be exposed to the mechanisms for generating new knowledge, rather than just learning lists of facts and the literature of the past. Witnessing the excitement of the research and discovery process tends to heighten student motivation and interest in the field. Although a Ph.D. is not required for one to be an active researcher, nor does it guarantee that one will be, most university departments have found that a Ph.D. degree does seem to provide the background needed to be research-active in one's field. Those involved in research also tend to keep abreast of the newest developments in their field, which helps keep teaching materials from becoming stale.

The Role of Ph.D. Training in the Conservation Field

Many of the functions served by Ph.D. programs in other fields also apply to conservation. Very few other degree-granting professional fields do not include the Ph.D. level in at least some representative universities. Those fields for which a master's degree is generally the terminal degree are almost exclusively in the fine arts, where practical work rather than research is the major goal. Examples are art, architecture, design, music, and theater. Some might argue that conservation better fits those models than it does the Ph.D.-populated fields such as chemistry, geology, or materials science.

However, we can also take the viewpoint that conservation does in fact differ from a field such as music, and in some important ways is allied more closely with applied technical fields such as medicine, veterinary medicine, psychology, and agriculture. Although treatment and preventive actions involve practical hands-on work, there is also a vital need for the constant development and careful assessment of new materials and techniques. In order to prevent damage to works of art through conservation efforts themselves, to more fully take advantage of new breakthroughs in allied academic fields and in industry, and to deal with ongoing changes in art materials and techniques, conservation requires a sophisticated experimental component. If we do not train conservators to develop, properly test, and report in an accessible written format new materials and procedures, then we are trapped into other choices:

- New ideas will emerge only slowly, if at all, and our profession will stagnate in comparison to other professions.
- New ideas that appear in our field will be applied to works of art without proper testing and evaluation through peer-reviewed channels; negative results can damage the reputation of the entire profession.
- We will rely primarily on scientists from outside the profession to author and test new developments for us. Identifying for them our greatest priorities, convincing them to spend the necessary time and expense on those problems, and trying to make their work understandable and accessible to practitioners in our field requires much effort.

Those institutions which have recently developed Ph.D. programs in conservation have recognized that, in addition to working with scientists outside of our field, we also need to take responsibility for educating those within our field who are attracted to research. Such individuals need not become full-time conservation scientists, but may well continue as practical conservators while becoming heavily involved in conducting research as well.

In addition to conducting or participating in research on conservation materials and techniques, conservators are also in a unique position to contribute to projects involving technical studies of works of art. Art historians receive training in traditional approaches such as iconographic and stylistic analysis and archival research. They seldom have any background in scientific methods. Scientists with little or no art history background are often unaware of the research techniques and types of information available through art historical methods. They may also have little knowledge concerning which problems are or are not considered by art historians to be of importance.

Certainly, we have many examples of art historians, conservators, and scientists working together as a team to solve problems requiring the addition of a technical approach. However, there is also room for an individual who has some in-depth background in both a subfield of art history and in one of the sciences. Most university departments in fields such as art history, chemistry, or geology do not have the flexibility to accommodate a student who might wish to take coursework in another unrelated field, or to do a dissertation with large sections involving research in a vastly different field. Conservators with Master's degrees in their field have already had to take many courses in studio art, art history, and chemistry; through their practical experience as conservators they spend much time closely examining works of art, including detailed studies of surface appearance and of production technology. Ph.D. programs within conservation departments can build upon this interdisciplinary background.

Finally, as in other fields, there is a place for art conservation Ph.D.s in university teaching programs. The opportunity for graduate students in conservation to have contact with research-active faculty provides the same beneficial effects widely recognized in other university departments. Since it has been difficult to obtain a Ph.D. in conservation, faculty have in the past received their doctoral competence in supporting areas such as chemistry and archaeology rather than within the core curriculum; in the future we can expect that graduate programs will add faculty with Ph.D. degrees in conservation with a variety of concentrations [6].

Research Qualifications of Ph.D. Conservators

One criticism that appears in discussions of the development of conservation Ph.D. programs is that students do not gain enough knowledge within any specific scientific discipline to conduct research at a high scientific level. I reject that criticism on several grounds:

- It is true that chemists and materials scientists with a greater depth of knowledge and experience in their fields will be able to contribute towards the development of new materials and techniques for conservation in ways that conservators cannot. However, we must not forget that one-half of the specialty called "conservation science" is "conservation." This implies that those whose primary training and practical experience is as a conservator can, in turn, contribute to the development of the field in ways that non-conservators cannot. Both types of researchers are needed for optimum advancement of our field.
- Most students should in fact be able to gain in-depth knowledge in a specific area of research. Certainly, some conservators have little background in laboratory science, and they will have difficulty acquiring the expertise needed for quality research. However, other conservators may enter a Ph.D. program with strong experience in laboratory research.

There is a general misconception that practicing conservators receive little or no training in laboratory science. To the contrary, the entrance and degree requirements of graduate programs in conservation ensure a relatively strong laboratory background. For instance, one of the entrance requirements of the M.S. program at the University of Delaware/Winterthur Museum is two years of chemistry with laboratory experience, including both inorganic and organic chemistry. During the first two years of the graduate program students take four more courses, including analytical chemistry, conservation science,

and an independent research project. Graduates of the University of Delaware/Winterthur M.S. program in conservation thus will have taken a *minimum* of eight semesters of chemistry.

To this basic foundation, Ph.D. students add courses and laboratory experience in the areas they wish to emphasize for their dissertation research. Such students should therefore be qualified to carry out scientific research. Probably the greatest factor in determining how much remedial work in science will be required of a Ph.D. student is the length of time that has elapsed since graduation from the Master's program, and how much laboratory work the conservator has continued to do during the intervening period.

The art historical background needed for carrying out advanced research also receives a good foundation through the entrance requirements and/or the coursework requirements of graduate programs. For example, the University of Delaware requires six upper division courses in art history or archaeology for entrance, and students take two more graduate-level art history seminars while in the program. Additional advanced coursework is required of Ph.D. students. With this background, students should be able to define art historical problems that can be addressed by technical studies and to provide some original contributions and insights from the art historical perspective as well as the technical.

- It is true that art conservation Ph.D.s will have less expertise in their chosen laboratory science than will Ph.D.s trained only in a science field; it is also true that they will know far less art history than Ph.D. art historians. This situation is to be expected, given that art conservation students must cover both areas, and will also continue to increase the depth of their knowledge and practical experience in conservation treatment. Nevertheless, true expertise can be developed as long as one is realistic about the range of that expertise. For example, an art conservation Ph.D. student researching a nineteenth-century American painter might study American painting and sculpture of that century and become adept at performing and understanding optical microscopy, scanning electron microscopy, x-ray diffraction, and several methods for identifying organic components. Doctoral students in art history and chemistry departments would each gain expertise in broader areas within their field.
- Graduates of Ph.D. programs in conservation should be qualified to serve as co-principal investigators with scientists in other fields. Collaborative research involving diverse talents is common in many other fields. Conservators who are trained in research design through a Ph.D. program, have research expertise in one or more areas, and are able to contribute towards interpretation and writing of results, will be better contributors to interdisciplinary research.

Historical Parallels Between Conservation and Materials Science Ph.D. Programs

An assessment of the role of a Ph.D. degree in the education of a conservator is strongly connected to discussions of the development of the subfield of conservation science. It is interesting in that regard to take an historical view and examine discussions that took place as "materials science" emerged as an established discipline [7]. The first academic programs in materials science were seen by some to be a horrible dilution of topics. Physicists felt that there was insufficient physics in the curriculum for graduates to be competent in their subject, metallurgists felt that the training given in metallurgy was far too shallow, as did the polymer scientists, etc. Many scientists were pessimistic that such an interdisciplinary type of program could produce graduates who had enough depth of knowledge in any particular field to conduct high quality research. Now, many years later, materials science is a recognized discipline and a separate department within many Ph.D.-granting universities. As a profession, it has funding through the National Science Foundation and other agencies, and a number of specialized journals. Many researchers with a Ph.D. in materials science are making important scientific and technical contributions. The desir-

ability of separate departments with academic programs leading to the Ph.D. degree in materials science is now unquestioned.

Stanley Warren [7], in talking about the allied area of archaeological science, noted that university programs should be working towards creating students capable of an interdisciplinary rather than a multidisciplinary approach. He urges us not to be afraid to produce archaeological scientists in the future, since other academic areas are already producing graduates from interdisciplinary courses of study (such as environmental science, earth science, and materials science). Conservation science might be seen as a logical extension of his observations. One would also expect that the transition from a multidisciplinary viewpoint to the more integrated interdisciplinary one should be easier for a graduate from a program requiring studies in at least two fields than it should be for a team of individuals each with backgrounds in single fields.

Conclusions

Adequate training in research methodology at the Master's degree level is difficult, because of the scarce time available in the curriculum in light of all of the practical conservation work that must be covered. (The practical, hands-on training is, after all, the first priority of such programs.) The best we can hope to do is to introduce the subject, provide some research and writing experience, and teach students how to critically evaluate the literature and presentations of new materials and techniques that they may encounter. In other practical fields a Ph.D. level has evolved to meet the specific educational needs of those few individuals who wish to curtail some of their practical work in order to emphasize original research. Our field is not uniquely different from all other fields, and a Ph.D. degree in conservation can have an important place here as well.

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Abstract

Establishing a conservation training program in the Netherlands for paintings and painted objects was a long and complicated process, whereas training in the fields of furniture, textiles, paper, and glass and ceramics already existed.

Keywords

Training, paintings conservation, interdisciplinarity, policy, Central Laboratory for Objects of Art and Science, Opleiding Restauratoren, Stichting Restauratie Atelier Limburg

A Training Program for Paintings Conservators in the Netherlands

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with an introduction by Willemien 't Hooft,
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Introduction

When the Limburg Restoration Atelier Foundation (Stichting Restauratie Atelier Limburg) in Maastricht decided in 1988 to open its doors for students to be trained in the conservation and restoration of paintings and painted objects, it was the right moment to open negotiations on co-operation between the State Training School for Conservators (Opleiding Restauratoren) and this foundation.

Up to that moment the conservation training programs taught at the Opleiding Restauratoren included furniture, textiles, books and paper, and glass and ceramics. These programs were geared to meet the need for trained conservators in the museums, archives and libraries of the Netherlands.

In 1977 when the Opleiding Restauratoren was established under the Ministry of Culture, Recreation and Social Work, the decision was taken to start a training program for the conservation of objects composed of natural polymers. Such objects suffer most from damage caused by light and the fluctuations of climate. A program on the conservation of glass and ceramics was added due to the dearth of trained conservators in this field.

It has always been the policy of our training programs that the number of students should meet the number of places available on the market. By "market" is meant conservation laboratories and/or studios in museums, archives, libraries and the private sector.

It cannot be denied that a gap threatened to develop in the field of paintings and painted objects conservation. Therefore the Ministry of Welfare, Public Health and Cultural Affairs eagerly responded to the initiative of the Province of Limburg which was clearly encouraged by Anne van Grevenstein. In 1989 a mutual agreement was signed by the Limburg Restoration Atelier Foundation and the Opleiding Restauratoren.

The Opleiding Restauratoren is ultimately responsible for the program and the students receive a diploma issued by the Netherlands Ministry of Welfare, Public Health and Cultural Affairs. However the Limburg Restoration Atelier Foundation is directly responsible for the form and content of this painting conservation training program.

Recently the so-called "Delta Plan for the Preservation of the Cultural Heritage" was presented by the Minister of Cultural Affairs. Part of this Delta Plan involved the creation of a national inventory of conservation backlogs. The figures and the seriousness of the situation made the politicians shudder at the very thought. In the spring of 1990, the government therefore decided to allocate a substantial extra sum for the preservation of the Netherlands' cultural heritage. Training also received extra funds from the Delta Plan budget. Conservators will be responsible for carrying out the work needed to address conservation backlogs, and they will also supervise the activities of maintenance staff in museums, archives and libraries.

There is clearly a need for properly educated and highly trained conservators who are able to tackle complicated conservation problems and who have a complete understanding of the complexities involved in the care of collections as a whole.

In co-operation with scientists, art-historians and maintenance staff they put up the good fight for the ideal situation which will hopefully prevent our cultural heritage from decay and save it for the education and pleasure of our children and grandchildren. Our task as educators is to match training in conservation with job requirements.

A Brief Historic Survey

The earliest plans for training paintings conservators in the Netherlands were conceived in the late fifties by a group of museum directors with the Director of the Rijksmuseum in Amsterdam, A. Van Schendel, as the main driving force. This was a period in which institutes for research in painting techniques were combining restoration, research and training within an interdisciplinary structure, and efforts for international collaboration between research institutes were developing due to the role of leading personalities like P. Coremans, G. Stout, W.G. Constable and I. Rawlins. This formed a fertile climate for the genesis of the Central Laboratory in Amsterdam.

The Central Research Laboratory for Objects of Art and Science

This institute was founded in 1962 to function as a center for research, restoration and training. Ir. J. Lodewijks was commissioned by the Ministry of Cultural Affairs to draw up plans to provide well-trained young museum personnel, who would eventually be capable of taking over the jobs of their aging teachers.

The Association of Museum Conservators and Technicians (founded in 1963) supported the plans and together with the Advisory Committee of the Central Laboratory also proposed to upgrade the salaries of existing museum personnel (1).

In 1964 the Ministry of Social Affairs rejected the plans of the State Secretary of Cultural Affairs, because of the unacceptable financial consequences. Plans for training new conservators without upgrading the status of existing museum personnel were understandably criticized. Further discussion between the Central Laboratory, the Association of Museum Conservators and Technicians and the Ministry of Cultural Affairs led to the latter's announcement in 1969 of the creation of a School for Conservation in 1970. The Director of the Central Laboratory proposed to provide high-level training for young conservators with the assistance of foreign specialists and to organise courses at a lower level for technicians (2). The involvement of the existing workshops in the Museums was rejected because it would entail too much diversification in the learning program.

In 1970 Ir. J. Lodewijks appointed E. van de Wetering, an art historian and painter, as head of the training program. Museum directors and staff firmly opposed the proposed plans for training conservators for the following reasons: the curatorial staff was reluctant to share the responsibility of decision-making with the new conservators, preferring to maintain clear lines of authority over staff conservators who, in turn, were still on shockingly low salaries and therefore deeply resented the idea of an influx of better-paid newcomers.

Training for Existing Museum Conservators at the Central Laboratory (1970)

Sensitive to these problems within the field of conservation, E. van de Wetering reconsidered his position and probably very wisely advised the director of the Central Laboratory to organise courses for existing museum personnel first (3). He proposed an "open structure" for training conservators, involving the participation of many museum workshops and with various other training forms according to individual needs.

This was taken on by an independent Foundation for the Education of Conservators which advocated an interdisciplinary approach to conservation problems. Mainly in the field of textile and paper conservation, this formed the basis for future progress and collaboration. Painting conservators, for whom these courses were also intended, rarely attended and remained in splendid isolation.

The State Training School for Conservators

With the appointment of the art historian M. Kirby Talley Jr. as head of the State Training School for Conservators for Conservation in 1977, this situation was further accentuated: the decision to train conservators of 'natural polymers' as all-round museum personnel obviously avoided the issue of training paintings conservators.

The policy of training all-round conservators was abandoned with the appointment of the new director Ms. W. 't Hooft in 1984 and good specialized training programs in the fields of textile, paper and furniture conservation were developed. Craftsmanship and aesthetic appreciation ranked high among the aims of the State Training School for Conservators and it became an independent institution from the neighbouring Central Laboratory.

Paintings Conservation in the Eighties

During previous decades, initiatives undertaken to provide institutionalised training in paintings conservation had failed and in the meantime nearly all official jobs for paintings conservators in the museums had been filled by well-trained restorers from Germany, Austria, Denmark, the United Kingdom, Italy, the United States, Belgium and France.

In the second half of the eighties a parallel group of young Dutch trainees, apprenticing in private studios and in museums, continued to struggle for their basic education and were applying for admission into courses outside the Netherlands. The need to organize something for them in their own country (if only to help them get admitted to one of the foreign schools!) was strongly felt.

On the initiative of the Paintings Conservation Department of the Frans Hals-museum, painting conservators met for the first time at the Central Lab in April 1986, having found in the new Director Ms. A. Gräfin Ballestrem, a stimulating and sympathetic colleague. The coordination work was taken over by the provincial Limburg Restoration Atelier Foundation in 1988.

During the two years which followed this meeting, a one-day-a-week program of theory was organized for the young Dutch trainees at the Central Lab including climatology, chemistry, history and ethics of restoration as well as drawing lessons.

In 1988 a three-week course in historical painting techniques was organized for the same group of young Dutch restorers at the Abbey of Rolduc in the south of the Netherlands, with such guest teachers as Beate Federspiel (Danish School for Conservation), Karin Groen (Hamilton Kerr Institute), A. Wallert (now the Getty Museum) and E. van de Wetering (University of Amsterdam). All these activities were forerunners of the formal training program that was to start in September 1990.

The Training of Paintings Conservators at the State Training School for Conservators

The Working Group of Museum Conservators (4) agreed to contact the State Training School for Conservators about setting up a new course within their program. A working contract between the State Training School for Conservators and the provincial "Restauratie Atelier Limburg Foundation" was signed to this effect in June 1989.

In the two years preceding the start of the training program, intensive contact was sought among various working groups of conservators to try to establish a broad consensus on the criteria to be applied to this new training program for paintings conservators.

The IIC-Netherlands Working Group on Training

The IIC-Netherlands Working Group on Training was founded in 1977 (5). In 1979, the Working Group had reviewed the plans of the State Training School for Conservators – an institution under the Ministry of Cultural Affairs. In a report for IIC members (April 1980) the Working Group had expressed

the wish for the training to be under the formal responsibility of the Ministry of Education, on the level of "higher professional education". The training should lead to the recognition of the profession as such (no longer as a craft) and raise the incongruously low salary level for state employees.

In March 1989 (6) the IIC working group met again to discuss the new plans proposed by the museum conservators and thoroughly examined the various possibilities still offered by other educational structures. The requirements of the 1980 report were unchanged; however, a combination of the fact that the State Training School for Conservators had been officially recognized by the Ministry of Education (which now issued an official diploma) and that finance and organization were satisfactory, and, finally, due to the wish of many IIC members to get "something started", a majority of members agreed to send a delegation of the IIC-Netherlands group to the meeting of the Advisory Committee.

The Advisory Committee

The Advisory Committee (7) to the "Training for Conservators of Paintings and Painted Objects" was set up by the Minister of Culture and met for the first time in 1990 to examine the curriculum and general organization of the project. Useful suggestions of the working groups and the members of the Advisory Committee were included in the final version of the curriculum.

The Training Program for Paintings Conservators

The past 30 years have taught us how vitally important a coherent balance can be between the field of conservation, museum management and the organization of a training program, or rather, how paralysing the lack of communication can be for progress.

When in 1989 plans were once again made for a training course in paintings conservation, the situation was quite different: the initiative came from the museum studios that were trying to combine restoration projects, research and training. Information aimed at the public about what goes on behind the scenes served as an impetus for consciousness-raising in the field of conservation. Museum visitors were thrilled by the technical aspects of artistic creation and by the ethical and aesthetic issues in the conservation world. Exhibitions, restoration projects, publications and TV productions had shown what interdisciplinarity was all about. The professional input of conservators had been essential during large international exhibitions and this favoured communication between museum management and technical personnel.

The image of the conservator had of course also changed in those years. Restorers of the past generation had often been artists who had taught themselves conservation techniques through autodidactic means. Frustration towards the successful creative artist and towards the academic museum management, combined with the poor salaries received by state employees, were in sharp contrast to the emerging perception of conservation as a difficult and highly responsible job.

The professional profile of the newly appointed conservators was much better defined through training within an organized framework in foreign schools. Being the last country in Europe without formal training for paintings conservators, the Netherlands was able to benefit from lessons of trial and error in foreign schools.

Heading undoubtedly for their own national mistakes, painting conservators agreed on the desirability of:

- a five-year course at a post-academic level
- one level of education rather than splitting the job into higher and lower responsibilities
- a chronological curriculum combining conservation practice, conservation science and painting technique within an art-historical framework
- a firm integration with museum practice
- the combination of a permanent setting (conservation studio and scientific department) and guest-teachers

- basic training during the first three years and internships in at least three museums in the fourth and fifth years

The Basic Years in Maastricht

The setting for the training is a provincial workshop (Limburg Restoration Atelier Foundation) with a permanent staff of three painting conservators, one sculpture and one paper conservator and a scientist thoroughly acquainted with interdisciplinary dialogue.

Stability in the first three years is assured by the availability of a wide range of objects within public collections that can fit into a chronological curriculum, combined with a permanent production workshop with good restorers and craftsmen and a scientific department carrying out high quality research. This stability is essential to achieve integration of both conservation practice and theory. In this way attention can be focused on the objects to be restored in the atmosphere of a real studio.

The mobile component, the guest teachers, provides quality and an obvious broadening of horizon. Some of them come for a day, others come for as long as three weeks or return at regular intervals. All wisdom cannot come from one source and without this mobile element, institutional dogma would have a greater chance of developing.

The eight students each take on a different responsibility for the rest of the group in collecting and editing information given by the guest lecturers. Individual student research is regularly presented and a dynamic exchange of information between staff and students ensues.

None of the polychromed sculptures or paintings are treated as exercise objects; they are the full responsibility of the student, each of whom is expected to finish documentation, research and treatment within a given period of time. On the other hand, quite a lot of conservation work and research by members of staff is carried out around the students, as a shared experience.

Because of the selection criteria applied to students at the start (A-levels in chemistry and preferably a degree in art history) there is no need for general courses and theory can be organized at an advanced level within the chronological framework.

The background of all students is of course very theoretical, so it is necessary to invest a lot of energy in craftsmanship, especially at the beginning of the training. During selection procedures, the students are screened for a certain level of visual and manual ability. Their abilities are sufficient to enable them to participate in intensive woodwork, drawing and painting technique classes. At the same time, historical knowledge is integrated as fully as possible. For example, in the first semester of the first year during their woodwork class, the students make the panels for the exercises using historical painting techniques.

The first semester is also the only trial period for the students. After admission to the second semester and introduction to conservation technique, it is considered the staff's responsibility to keep the group "together". The museum conservators come twice a year to visit the workshop - first to get to know the students better. It is a good opportunity for the students to present their conservation work, documentation and research. They also report on didactic activities that have taken place. With the bi-annual visits of the Advisory Committee, students give a lively account of their work: to acknowledge growth in awareness and ability is a rewarding experience. At the end of the third year, a written and oral examination assesses the absorption of knowledge by the student.

Museum Internships

At the end of the third year, the chronological curriculum has reached the 18th century.

In the fourth year, which is split between two internships - six months in a

museum of modern art and six months in a museum of early pictures - attention will be focused on the 19th and 20th century. The organization of conservation work, research and the task of coordinating student projects in the museums will be taken over by the resident restorer of the Central Lab in Amsterdam, IJsbrand Hummelen. Research projects will continue to be monitored by Karin Groen, staff scientist at the Maastricht studio.

The fifth year will be devoted to one internship and a final conservation/research project; it will be the year in which the State Training School for Conservators examination is taken and the diploma is obtained.

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Stedelijk Museum
AMSTERDAM

P.J.M. Deuss
Dordrecht Museum
DORDRECHT

E. Hendriks
Frans Hals Museum/De Hallen
HAARLEM

A. van Grevenstein
SRAL
KERKRADE

L. Rutgers van der Loeff
Het Mauritshuis
THE HAGUE

M. Zeldenrust
Rijksmuseum
AMSTERDAM

J. Wadum
Het Mauritshuis
DEN HAAG

N. Newman/F. Verberne
Rijksmuseum Twenthe
ENSCHDE

M. Broekema
Opleiding Restauratoren
AMSTERDAM

C. Pérès
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Gogh, AMSTERDAM

IJ. Hummelen
Centraal Laboratorium
AMSTERDAM

G. Tauber
Rijksmuseum
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5. Members of the IIC Working group on training, 1977: J.R.J. van Asperen de Boer, C.M.A. Dalderup, A. van Grevenstein-Kruse, P.F.J.M. Hermesdorf (+), H. Janse, M.L. Wurfbain.

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Abstract

The definition and historical context of conservation technicians in the UK is reviewed. Normally, technicians are expected to carry out practical work to support specialists. Examination of the thought processes required to carry out most conservation practical work indicates that it is beyond a technical level. Several possible reasons for the recent re-emergence of the phrase conservation technician are suggested: changes in management attitudes; attempts to transpose the established technician/scientist relationship into a technician/conservator role without considering the needs of conservation practice; a genuine need for technical support for conservators. The role and remit of the conservation technician and the training required to meet this standard await definition. Unless they are defined soon, the professional standing of conservation is likely to suffer.

Keywords

Conservation, technicians, training, management, science

Conservators and Conservation Technicians: Definitions and Differences

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Introduction

Most professionals would provide differing definitions of a technician's role and status, but their opinion would be heavily influenced by national perceptions of technicians. I would define a technician as, "an individual who is trained, especially in practical applications, to support the work of more highly qualified professionals who interpret the end products of the technician's work."

Is this definition suitable to describe the work of a conservation technician? To answer this question, it is necessary to review the historical role of the technician in conservation practice, define the word "technician" and then discuss this in relation to conservation practice.

Conservation technicians in the UK: historical perspective

Prevailing attitudes within the museum world in the 1950s and 1960s labelled conservation as a technical/craft service and saw conservators as technicians. The standing of conservators within the museum hierarchy was low. Conservators were rarely, if ever, consulted on managerial decisions concerning the welfare of collections. Since there was no managerial parity with keepers and conservation departments did not exist, conservators tended to be attached to museum departments or sections, and were managed by section heads. Naturally, in some institutions, conservators either by force of character or via enlightened keepers and directors, did influence decisions concerning the welfare of collections.

This situation was slowly changed by the efforts of conservation bodies, such as IIC and UKG/IIC (now UKIC), individual conservators and training institutions, aided by a slowly growing recognition within the museum world that collections required specialist conservation management. Conservation departments, keepers of conservation, expansion of conservation facilities and, possibly most importantly, the virtual disappearance of the technician label, have been the result of progress. The standards now achieved in conservation practice and training are of a standard which cannot be given a technician label. Without the loss of this label, it is doubtful whether conservation could have progressed to the point it has now reached.

In the UK, the recent re-use of the term conservation technician, both in published papers (1, 2) and in general usage in conservation circles, has rekindled worries amongst many conservators concerning the status of the profession and the standing of the conservator. This terminology has crept back into usage without any concerted effort to define what it means or any exploration as to why it might suddenly be re-emerging. Associated with its usage is the question of whether a conservation technician is a lower grade of conservator. By implication this downgrades practical conservation to a more menial role, making it distinct from management levels. Currently there is a single category of conservator who is expected to have a certain base level of skill and knowledge (3). Experience qualifies individual conservators for higher grades of post.

What is a technician?

Perhaps the easiest way to address this question is to turn to technicians and their employers for an answer.

A review of university technicians provides an insight into the work of technicians across a broad range of disciplines. Whilst the nature and complexity of a technician's work differs, according to both the discipline and the grade of

the post, there must be some underlying general principles which define the work as technical. Since universities are at the top of the educational ladder, the demands of teaching and research must mean that university technicians are amongst the most highly trained and skilled technicians. In an attempt to determine the maximum performance expected of a technician, the remit of selected higher graded technical posts in the university sector is examined (4).

A points system is used for grading university technician posts. Points are awarded for educational qualifications ranging from General Level Certificate of Education, taken at age sixteen (level 1), to university degrees which are given the highest grading (level 4). Sensibly, as in many other professions, these qualifications are linked to experience, ranging from 1 year (level 1) to 10 years or more (level 5). Grading also relies upon work complexity, responsibility for staff and equipment, physical strain and many other typical job evaluation factors.

Interestingly, the Job Evaluation Manual (4) covers nine basic disciplines and fifty-three separate technical jobs, but not a single post requires the holder to possess a university degree. It is worth examining two posts from different disciplines to determine what factors are common to the job description of a technician. Tables I and II show the job remit of a grade D Laboratory Technician Supervision (Research) and a grade D Horticultural Technician. (The top technical grade is effectively G and is an administrative post and requires greater management skill).

Table I. Science Laboratory Technician (Research) grade D.

-
1. Operation and maintenance of complex and sophisticated research apparatus, equipment and instruments, etc., spectroscopy and chromatographic instruments and techniques in molecular determination for research and analytical purposes.
 2. Development modification and construction of special equipment and apparatus for research purposes using specialised techniques.
 3. The setting up of experimental apparatus and research systems and the development of new or improved methods under supervision of academic staff or higher graded technical staff.
 4. Preparation and collation of results for interpretation.
 5. Assistance to students in the design (i.e. the methods and planning) of research in experiments and in particular applications of equipment used.
 6. Instructing technical staff in laboratory techniques and in the operation of particular equipment/apparatus as directed by a supervisor or member of staff.
 7. Mixed supervision of other technical staff as appropriate.
 8. Preparation of special solutions, chromatographic plates, purification of solvents.

Education: level 3.

Experience: 7 to 10 years

Table II. Botanical Technician (ii) (Research). Major activities and responsibilities.

-
1. Preparation and sterilisation of botanical media and manufacture of stock cultures in sterile conditions.
 2. Analysis and estimation of samples using precision techniques; flame photometry, atomic absorption, spectrophotometry etc.
 3. Calculating and tabulating results.
 4. Laying out and checking the preparation of apparatus and media for teaching purposes.
 5. Checking the working conditions of apparatus and equipment.
 6. Checking general laboratory tidiness.
 7. Training of technical staff to use equipment and laboratory techniques.
 8. Provision of assistance and advice to research students and demonstration of specialised techniques.
 9. Maintenance of cost records where necessary and as directed.
 10. Limited occasional supervision.

Education: level 3.

Experience: 7 to 10 years.

Comparing the posts provides some interesting conclusions which are relevant to discussions on conservation technicians:

- (a) None of the posts requires the holder to interpret results, although "preparation and collation" (table I), "calculation and tabulation" (table II) of results are asked for. This shows a clear limit on the extent of lateral thinking expected from a technician. Which is, perhaps, why degree level education is not required for any technician post, and should a degree holder occupy a technician's post, they may be frustrated by the limitations of the work.
- (b) A glance at tables I and II, shows that there are a broad range of tasks relating to the operation and maintenance of equipment, occasionally demanding innovation in the operation of equipment. This necessitates a sound practical working knowledge of the equipment in question and an ability to understand manuals very effectively.

In summary, technicians would appear to be required to operate and service a broad range of equipment, obtain results from experiments and carry out support work for academics or specialists. It is also clear that the technician is expected to possess skills in data collection, but that the interpretation of analytical data is not within their remit. An academic does this, using a broad range of hypotheses to create a dynamic interpretive process.

The role of conservation technicians

No one has tried to provide a reasoned and ordered definition of the technician's role in conservation. Discussion is therefore based on the few published opinions and personal viewpoints.

Cronyn and Pye (1) see the conservation technician as an essential component of their structure for the profession. The duties of these technicians are not detailed, other than defining the technician as someone "who provides practical routine support for the conservator and/or conservation scientist". This broad generalisation does not indicate whether practical conservation work on objects will be entrusted to the technician. Oddy (2) defines the present role of technicians in the British Museum as "support duties, such as making mounts, maintaining equipment and supplies and in dusting sculpture." He continues by stating "In some UK National Museums they are also involved in the routine cleaning of metals, ceramics, stone etc. and in the simple repair of library books." This is less clear cut technical work since the definition of routine practical work is not provided and may be a contentious issue.

The general laboratory duties required of any technician in a science setting are easy to define. The range of tasks which a trained conservation technician could be expected to carry out on objects would be difficult to define.

Environmental monitoring may be considered a job suitable for a conservation technician, as it is not "hands-on" practical work. An examination of the possible role of the conservation technician shows that it is limited to the installation, operation and repair of the monitoring equipment. Interpretation of the results produced by environmental monitoring must lie with the trained conservator. This is due to the vast amount of background knowledge required to apply the results to artifactual material. Here the role of the conservation technician can be paralleled very closely with that of the science technician, as a data collector and machine operator.

It is often suggested that conservation technicians could be instructed and supervised by a trained conservator, for work which requires the knowledge/training of a conservator. This could create a dangerous precedent, such as with the word 'cleaning'.

Routine cleaning is a favoured term in relation to the type of work a conservation technician might carry out, yet cleaning itself has many definitions. Consider archaeological conservation: the investigative cleaning of any archaeological metal requires a sound knowledge of corrosion science, metals technology, burial environments, archaeology and, importantly, excellent investigative and interpretive skills. The identification of processes such as tinning, soldering and the

detection of 'original' surfaces requires highly developed powers of observation, an ability to cross reference data and develop theories. Because two or three hundred objects have to be dealt with, the practical work involved can, erroneously, be described as routine. Most of the archaeological conservators I have spoken to are of the opinion that no technician would be capable of carrying out this work to the same standard as a trained conservator, even under close supervision. During investigative cleaning, observation, questioning and recording is a continuous process. The thought process required is not unlike the dynamic interpretive process mentioned in relation to the interpretation of results. Objects are unique and, if the technician has insufficient knowledge to identify the data being uncovered or to formulate the correct questions for the supervisor, it is too late to rectify any error as the information will have disappeared unnoticed. Added to this is the fact that an overall conservation rationale underlies all the decision-making processes of the conservator. This cannot be taught piecemeal, as the UKIC core syllabus acknowledges (3). It is part of the degree level training package which all archaeological, and many other, conservators have.

So what level of practical work could conservation technicians be expected to carry out without supervision? This could be answered by asking a simple question related to universally accepted standards of conservation training in the UK, "When does the level of knowledge required to carry out a conservation task on an object, require the practitioner to possess the content of the UKIC core syllabus for conservators (3)?" If this level of training is required for the task, then, by definition, the work lies within the remit of a trained conservator. It is clear that an ability to physically execute practical work is not a licence to implement that work. It is also necessary to know why the work is being carried out and to support this with the necessary underpinning knowledge.

Looking at these few examples highlights the problems evident in defining the role and job remit of conservation technicians. Much discussion, involving the full range of conservation bodies and teaching institutions, is needed to define the role of conservation technicians and the training they will require. This is a prerequisite of the usage of the terminology in modern conservation practice in the UK.

Why has the term conservation technician re-entered the conservation vocabulary?

A number of reasons can be advanced to explain why this has happened.

First, it may be possible to attribute it to the growth of a totally different work ethic and management style in the 1980s. Management has become an industry in itself, complete with a whole new language of its own, with new words or phrases for each of the tasks and parameters that have always been a part of good management. In the UK, along with this language has come privatisation, financial pressure and a desire to economise. Economies can be achieved by increased workrates, reduced staff and lower pay. Ethics and professional standards mean that the concept of increased workrates is rarely deemed appropriate for conservation practice. Alternatively, in conservation, reduced staffing levels will normally mean less work output. A third possible approach is to redefine job descriptions downgrading work to less qualified and thus lower paid staff. In conservation this might be achieved by redefining certain aspects of conservation work as technical. It is hoped that management would not consider this to be an option.

Another factor may be due to the increased role of science in conservation. A close working relationship with scientists has improved conservation practice and research. In response, an increased science content in some conservation courses has been accommodated by making a cut in practical content. Also, scientists with no conservation training, have been drawn into senior conservation posts in teaching institutions and museums. In keeping with their background, scientists may have unknowingly brought into conservation the concept of technicians carrying out "hands on" practical work with the conservator directing, coordinating and interpreting the work. It is easy to see how non-

conservators may see this science blueprint as being directly applicable to conservation, but this interpretation ignores the depth of training which is required for what appear to be straightforward practical tasks.

During the past ten years, conservation management has increasingly become an area occupied by managers without conservation training, as recognised by a number of authors (5, 6, 7). Where managers lack conservation training, it is necessary to ask whether there is a gulf developing between managers and conservators, with management unable to recognise that practical work is not automatically at technician grade? It is hoped that this is not the case.

Taking a positive approach, carefully defining the role of conservation technicians would mean that they have a lot to offer conservation. Rather than downgrading conservation practical work by introducing a new lower level of conservator, technicians could provide valuable laboratory support to conservators. This supportive role is yet to be defined but unless it is, there will continue to be professional dispute regarding conservation technicians, with misunderstandings, mistrust and concern continuing to grow.

The status of technician as a job grading

The definition of a technician may differ according to the country in which the terminology is being used. This paper has addressed the use of the term in the UK, where "technician" is not synonymous with the terms "professional" or "profession". To have technicians carrying out interventionist conservation work, which has previously been argued as being within the remit of the trained conservator, could be interpreted by management and other professionals as a sign that conservation is a technical service rather than a profession.

In other countries, such as Denmark, the term "conservation technician" must clearly have a different meaning (8). The School of Conservation there takes three years to train conservation technicians and five years to train conservators. The conservation technicians produced must be highly qualified. In the UK, three year courses produce conservators who are seen to lack only experience, rather than basic training. Yet the role of the technicians does not seem to be clear cut as Beate Federspiel (8) asks, "Should routine work be carried out by technicians and not graduates? If such a thing as 'routine work' exists in our field, an arrangement like that would no doubt create a bad atmosphere in a workshop."

Finally, conservation technician grade posts do exist in the UK. Although their exact remit and the qualifications required to fill them may be clear within individual institutions, these remain unclear within the profession as a whole. Sometimes the terminology is used to control salary grades and post holders are expected to have conservation qualifications. In other instances the post holder may have had no formal conservation training but is effectively carrying out the work of a conservator, either because they have been in post for many years or because the salary scale does not attract a professional conservator. In all of these instances, a clearer definition of what is considered to be technical work in conservation, would benefit the post holders and the profession.

Conclusions

Perhaps the most important conclusion is that, for the most part, conservation theory and practice are indivisible. The minimum level of acceptable training for a conservator (3) dashes the idea of a two tier level of conservator, separated by theory and practice.

Therefore the conservation technician has a limited supportive role to offer the conservator. They cannot provide the same degree of practical support as, for example, that which a science technician provides to the scientist, because the nature of conservation practical work is so radically different to the operation of scientific equipment. Consequently, the influence of science on conservation should not extend to viewing practical conservation as being within a technician's remit merely because of its practical content.

Economic considerations should not influence management practices to the extent that the conservation practical work is downgraded for financial reasons. Conservation managers should always be well versed in conservation thinking and practice, in order to maintain a full understanding of the structure and challenges of the profession.

The nature of the technical support required by conservators is in urgent need of clarification.

Several suggestions for immediate action are made.

1. Create an international committee to define the role of the conservation technician.
2. Define the content of a training scheme for conservation technicians.
3. Discuss methods of implementing training schemes.

In Britain, these points are particularly urgent in the context of the grading and structuring of conservation which is taking place under the banner of the National Vocational Qualification scheme.

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Working Group 22

Metals

Métaux



Abstract

Analysis of the extent of corrosion of cast iron cannon recovered from historic shipwrecks off Australian coasts has revealed a common corrosion mechanism. Data obtained relate to cannon cast in the seventeenth and up to the nineteenth century with immersion times up to 366 years. Analysis of the kinetics of chloride ion extraction during storage and electrolysis in sodium hydroxide solutions has led to the development of a model for predicting the rate of the chloride extraction process. In-situ corrosion measurements relate the amount of water movement with the average corrosion rates and the depth of graphitisation of the cast iron cannon. Equations have been established that relate the depth of corrosion and the time taken to reach plateau levels. The amount of chloride ions removed and the rate at which the process occurs are intimately related to the nature of the shipwreck sites. Through the use of the relationships established from treatment of twenty six cannon from ten wreck sites it is now possible to calculate when treatments are likely to be completed and how much chloride ions will be able to be extracted in the conservation programme. With a knowledge of in-situ corrosion data it is now possible to establish which cannon will be in the best state of preservation prior to any recovery operation. The chloride extraction kinetics can also be used to calculate the age of unknown shipwrecks!

Keywords

Corrosion, conservation, iron cannon, treatment kinetics, shipwrecks, sea water, dating

Conservation of Corroded Iron Cannon and the Influence of Degradation on Treatment Times

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Introduction

One of the problems commonly encountered with the treatment of corroded iron cannon recovered from historic shipwreck sites is that it is very difficult to predict how long the treatment will take. Many of the concerns relate to the fact that for a number of conservators the object in front of them is the first example of such a massive artefact. Since corroded iron cannon have been undergoing treatment in the laboratories of the Western Australian Museum for the last twenty years there exists a considerable data base of treatment reports. Apart from laboratory studies, data obtained from in-situ corrosion measurements on ten wreck sites has also been collected to help find answers to the questions of how to treat the cannon.

When iron cannon are immersed in the warm tropical to sub-tropical waters they become colonised with a variety of marine organisms that form a protective and encapsulating layer of calcareous material over the surface of the object. The concretion consists of a matrix of corrosion products, marine organisms and the materials resulting from their interactions as well as entrained sediments. The process of concretion formation on iron objects has been described by North¹. More recently the increase in the rate of concretion formation due to the phosphorus content of the iron has been quantified². Analysis of the thickness of calcareous materials showed that there was a linear relationship between the annual growth rate and the weight percent phosphorus in the metal. The concretion layer forms a separation barrier between the oxidation of the artefact and the reduction of dissolved oxygen.

Recent in-situ studies of corroding iron artefacts on the wreck of HMS *Sirius* (1790) have established that the corrosion of iron on shipwreck sites is largely dominated by the flux of dissolved oxygen to the concreted surface³. The physical protrusion of an object on a wreck site will therefore be of major importance in determining how much oxygenated sea water will flow past the object. For buried artefacts the anaerobic corrosion mechanism, (corrosion in the absence of oxygen) will be dominated by the cathodic processes which involve the reduction of water. The data reported in this paper relates primarily to cannon that have corroded on the seabed in well oxygenated waters.

Results and discussion

Cannon corrosion on wreck sites

The *Batavia* (1629) wrecksite is characterised by massive wave surges as the heavy swells break over *Morning Reef* in the Houtman Abrolhos Islands located some 70 km out to sea from Geraldton, Western Australia. A series of cannon were recovered during the main excavations seasons between 1972–1976 and brought to Fremantle for conservation treatment using electrolysis in sodium hydroxide solutions. The technique is essentially the same as developed for the conservation of cannon from HMB *Endeavour* (1770)⁴. As part of the routine assessment of the effectiveness of the treatment process, samples of corroded metal are drilled at the initiation of the treatment and towards the end and analysed for chloride ions.

The analytical data provides the conservator with information about the extent of the degradation and about the fabrication technology. The composition of cast iron cannon results in a metallurgical structure that consists of varying

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proportions of graphite flakes in a matrix of cementite, pearlite and ferrite⁵. When the cannon corrodes, the phases that have the highest iron content will be preferentially oxidised and this ultimately results in a corroded zone that is essentially *graphitised cast iron*. The corroded cast iron has lost most of its original mechanical properties but it still retains the original surface details and overall dimensions. The retention of the original surface is the primary aim of the overall conservation treatment.

Apart from several cannon from the *Batavia* (1629), a total of eight cannon were recovered in 1980 from the wreck of the American China Trader *Rapid* (1811), five from the remains of the whaler *Lively* (1810), three from the *Vergulde Draeck* (1656) and individual cannon from the sites of the *Trial* (1622), *Zuytdorp* (1722), *Fairy Queen* (1875) and the *Cumberland* (1830). Since the *Rapid* site was the first at which in-situ corrosion measurements were taken⁶, it is useful to initially look at data from this wreck since it also had the most accessible archaeological records. In order to facilitate comparisons of the rate of corrosion on a variety of sites that have been immersed in sea water for times varying from 114 to 365 years, the corrosion data is averaged over the number of years of immersion. The annual mean depth of graphitisation is noted as d_g in units of $\text{mm} \cdot \text{y}^{-1}$. Since corroded cast iron retains its original dimensions, the rate of corrosion can be gauged by measuring the depth of graphitisation of the cannon. This is effected by drilling into the artefact with a 5 mm. steel bit until the resistance of the uncorroded metal is felt—the depth of penetration, d , is the depth of graphitisation.

The *Rapid* cannon provide an interesting example of how the microenvironment on the site dictates the extent of corrosion. A summary of the data is listed in table 1. In assessing the data in table 1 it is useful to note that the average long-term corrosion rate for iron in a marine environment is approximately 0.1 mm per year⁷.

Table 1. Corrosion depths for cannon on the *Rapid* (1811).

Location	RP4090	RP4288	RP4031	RP4205	RP4206	RP4207	RP4147	RP4032
Muzzle*	16	17	10	4	10	14	4.5	12
Cascabel*	16	15	5	4	10	10	4	8
Mean*	16	16.7 ± 1.5	7.5 ± 3.5	4	10	12.0 ± 2.8	4.25 ± 0.4	10.0 ± 2.1
Annual d_g	0.096	0.101	0.045	0.024	0.059	0.072	0.026	0.059

* Corrosion/graphitisation depths measured in mm.

Inspection of the data in table 1 shows that two cannon from the *Rapid* had the "average" corrosion rate for an open ocean site. The wreck lies in seven metres of water inside an offshore reef and at the time of the initial site inspection only one cannon was seen lying proud of the sea bed. It is this cannon (RP4288) which is the most extensively graphitised. The carronade (RP 4090) with the higher corrosion rate was found under a mound of ballast. There were a significant number of copper artefacts located on the site in the general vicinity of the carronades. There were upwards of 850 copper artefacts within a two metre grid line found 6–8 metres from the guns. Copper fastenings in close proximity to the cannon showed significantly less corrosion than those artefacts further away.

Previous studies on the corrosion phenomena on this site^{8,9} and on the site of the *Hadda* in the Abrolhos Islands¹⁰ have confirmed the existence of proximity corrosion which is a form of long-range galvanic coupling. Such phenomena may be the underlying cause for the increased corrosion rate for the carronade RP 4090. Three other cannon were partially exposed on the seabed and they exhibited the next highest corrosion rate with an average value of the mean annual depth of graphitisation being $0.064 \pm 0.007 \text{ mm} \cdot \text{year}^{-1}$. Two of the cannon (RP 4206 & 4207) were a "crossed pair", i.e. they were found concreted together in a scissor formation.

The other two cannon (RP4147 & RP4205) and the two carronades (RP 4031 & RP 4090) were found under the mound of ballast stones and amongst the general wreckage of the vessel. The two buried cannon had an average annual mean corrosion rate of 0.025 ± 0.001 while the carronades had rates of 0.045 and $0.096 \text{ mm} \cdot \text{year}^{-1}$. Site excavation records are incomplete but the divers notes indicated that the carronades were placed at a higher level in the *sediment* than the cannon and this is reflected in the higher levels of corrosion. Generally it can be seen that, in the absence of specific effects of galvanic coupling, there is a lowering of the rate of corrosion with the increasing depth of burial on the site. This is primarily a reflection of the decreased amount of water movement combined with lower concentrations of dissolved oxygen.

Only one cannon (RP4205) had its corrosion potential ($E_{\text{corr.}}$) recorded on-site. The $E_{\text{corr.}}$ value was -0.412 volts (1) which indicated that it was corroding at a relatively slow rate. Using the relationship between $E_{\text{corr.}}$ values and corrosion on wreck sites³, the calculated depth of corrosion was $0.034 \text{ mm} \cdot \text{y}^{-1}$. The calculated value is within the range of the standard deviation of the observed rate of $0.024 \text{ mm} \cdot \text{y}^{-1}$.

The wreck of the *Lively* (c.1820) on the Rowley Shoals is characterised by a scattered deposit of metallic remains. No wooden structure remains and this is consistent with the much higher energy of the site. The wreck lies in a gully on the edge of a coral atoll and the water depth varies from seven to zero metres at the reef top. The corrosion parameters for the five cannon recovered from the site are listed below in table 2.

Table 2. Corrosion parameters for cannon from the *Lively* (1810).

Location	RS125	RS24	RS25	RS26	RS 124
Muzzle*	16	14	14	10	18
Cascabel*	12	14	10	10	16
Mean value*	14 ± 2.8	14.3 ± 0.6	12.0 ± 2.8	10	17.0 ± 1.4
Annual d_g	0.085	0.089	0.075	0.062	0.106
$E_{\text{corr.}}$ volts	-0.200	-0.262	-0.273	-0.252	-0.219

* Corrosion/graphitisation depths measured in mm.

Analysis of the corrosion potential data shows that there is a linear relationship between the corrosion potentials ($E_{\text{corr.}}$) and the logarithm of the average annual rate of graphitisation, i.e. $\log d_g$. The *in-situ* $E_{\text{corr.}}$ values of the cannon fall into two sets of data which have the same slope for the $E_{\text{corr.}}$ vs. $\log d_g$ plots but different intercepts. The equation is

$$\log d_g = 2.34 E_{\text{corr.}} - 0.459 \quad 1$$

for the cannon RS 24,25 & 124. For the RS 125 and RS 26 the intercept is -0.603 . It is possible that the difference in intercepts is due to some chemical or metallurgical difference in the cannon or that the nature of the water movement around these objects is different.

This logarithmic dependence of corrosion rate on the $E_{\text{corr.}}$ of the metal is consistent with corrosion phenomena that are under electrochemical control³. Each site will present a different range of corrosion microenvironments but since there is a direct linear relationship between the logarithm of the corrosion rate, as measured by $\log d_g$, and the $E_{\text{corr.}}$ value, it is now possible to see which cannon is the most/least corroded and so make the best archaeological decisions involving recovery.

Although no *in-situ* corrosion measurements have been made to date on the *Batavia*, the cannon recovered from the site have provided a useful set of ordnance that is generally extensively corroded. The physical nature of a shelving gully on the edge of a reef is typical of a high energy site characterised by large volumes of water flowing over the area with significant velocity. Large waves break heavily on the site during heavy ocean swells associated with storms etc.

Table 3. Depths of graphitisation of iron cannon from the wreck of the *Batavia* (1629).

Artefact no.	BAT 8731†	BAT 8722†	BAT 8723	BAT 8720	BAT 8724	BAT 8726	BAT 80309
Muzzle*	53	—	33	23	—	32	—
Cascabel*	63	44	54	48	29.2	16	18
Mean*	58 ± 7.1	44	43.5 ± 14.8	35.5 ± 17.7	29.2	24 ± 11.3	18
Annual d_g	0.167 ± 0.20	0.126	0.125 ± 0.043	0.102 ± 0.051	0.084	0.069 ± 0.033	0.052

* Corrosion/graphitisation depths measured in mm.

† The two cannon BAT 8731 & 8722 were both found broken on the wreck site.

It is not unexpected to find depths of graphitisation up to an mean value of 58 mm after more than 350 years of exposure to such conditions.

Although the range of average corrosion rates on the *Batavia* site is considerable, the variation from $0.167 - 0.052 \text{ mm} \cdot \text{y}^{-1}$ is of the same order as the range of rates found on the *Rapid* site. The major cause of variation on the *Batavia* site is the topography of the seabed which is full of local gullies and the piles of sandstone building blocks which resulted in localised turbulence. The smaller variations in d_g values observed for the cannon on the site of the *Lively* is due to the more localised distribution of the cannon. The average of the d_g values for the *Batavia*, *Lively* and *Rapid* sites are 0.104 ± 0.039 , 0.083 ± 0.016 and $0.060 \pm 0.029 \text{ mm} \cdot \text{y}^{-1}$ respectively. The shallower average water depth and the location of the *Batavia* and *Lively* sites on the edge of reefs is the primary cause for the differing extents of corrosion.

Data on the net effects of temperature on cannon corrosion are not unambiguous. Although the concentration of oxygen increases with decreasing temperature, the diffusion coefficients fall and so this often cancels out the apparent increase in the rate of supply of dissolved oxygen to the corroding surfaces. With cooler water the extent and nature of the marine growth also changes and this in turn alters the amount of "protection" that a concretion can provide. Two cannon from the site of the *Sydney Cove* (1797) in Bass Strait provide data from a much colder site. Although the site is subject to storms, it has a sandy bottom and the average water temperature is $14.5 \pm 2.3^\circ \text{C}$ at a water depth of 3–5.5 metres¹¹. The average graphitisation depth was $7.3 \pm 2.3 \text{ mm}$ which gives an d_g value of $0.041 \pm 0.013 \text{ mm} \cdot \text{y}^{-1}$ which is similar to one of the carronades on the *Rapid* site, where the average temperature is $24.4 \pm 2.0^\circ \text{C}$ ⁶.

Another cold site is that of the *Cumberland* (1830) off Cape Leeuwin where the average water temperature is $18.6 \pm 1.5^\circ \text{C}$ and the average annual corrosion rate was calculated at $0.028 \text{ mm} \cdot \text{y}^{-1}$. Again this corrosion rate is of the same order as two of the cannon from the *Rapid* site, where the cannon had been protected under the ballast mound. Observations on a large number of submerged iron materials indicates that the corrosion rate of concreted iron in sea water is relatively temperature independent¹².

Given that a common corrosion mechanism controls the deterioration of the cannon, it is not unexpected to find correlations between the amount of chloride ions extracted during conservation and the extent of corrosion. Analysis of treatment data for ten cannon from five sites, for which complete data sets are available, shows that the total number of kilograms of chloride ions is directly related to the depth of graphitisation, d , via the relationship

$$\Sigma \text{Cl} = 0.0367 d^2 + 2.61 \quad 2$$

where ΣCl is the weight of chloride ions in kg and d is the depth of graphitisation, measured in mm. Since the corrosion rate settles down to a pseudo steady-state after some years, it is not unexpected to find the parabolic relationship (equation 2) between the total amount of chloride in the cannon and the depth of graphitisation. Where cannon do not follow this relationship it is due to factors such as the *Zuytdorp* cannon having corroded only on the "outside" since the tompon in the muzzle had sealed the bore from the sea water². Equation 2 can be used to calculate the total amount of chloride that should be extracted from concreted iron cannon that have corroded in sea water where the salinity

ranges from 34–37 parts per thousand (ppt). Such calculations are a handy guide to conservators assessing the progress of an electrolysis treatment.

Chloride extraction rates

The diffusion controlled nature of the washing process has been well documented¹³ and it is noted that chloride ions diffuse out at a rate that is linearly dependent on the square root of the treatment time¹⁴. Once a plateau has been reached it is time to change to a fresh solution of sodium hydroxide. The chloride ions then diffuse out at a slower rate until the next plateau is reached and the solution changed again. Regular monitoring of the wash solutions of the cannon has provided the basic information as to when solutions need changing and when the treatment is complete. Many of the electrolysis times are in excess of five years. At the end of the electrolysis process the total amount of chloride ions released can be calculated from values of the plateau levels (corrected for background levels of the water) and from a knowledge of the solution volume.

We have applied the same methods of data analysis as for the desalination of copper and its alloys¹⁵ where the release rates were standardised as $\text{mg} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$ by multiplying the rate in ppm of chloride per hour^{1/2} by the solution volume in litres and dividing by the geometric surface area of the cannon in cm^2 . It should be noted that the contribution of surface roughness and effective porosity have been ignored in the calculations owing to our inability to accurately assess their values. The common microstructure and composition of the iron cannon means that corroded cannon are closely related in their physical properties. Analysis of the wash data for fifteen iron cannon shows that the rate of release of chloride ions is directly related to the "porosity" of the corroded metal via the relationship

$$R = 3610 d_g^2 - 0.110 \quad 3$$

where R is the chloride ion release rate in $\text{mg} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$ and d_g^2 is the square of the annual average depth of graphitisation of the cannon (in $\text{mm} \cdot \text{y}^{-1}$). Even though the more corroded cannon have a significantly greater amount of chloride ion in the corroded matrix, the rate of release is dependent on the tortuosity of the diffusion path.

With a knowledge of the depth of graphitisation and the time between when the vessel was wrecked and when the artefact was recovered, it is now possible using equations 2 and 3 to calculate not only the amount of chloride that can be expected to be released into the treatment solutions, but also the rate at which the ions will diffuse into the wash solutions. The relationships allow estimation of electrolysis treatment times and to assess whether or not the physical set-up of the electrolysis is optimal.

When the concentration of chloride ions at the plateau levels are compared with the total amount extracted by the end of the treatment some common relationships are found. The expressions for the percentage of chloride removed at each of the washing stages is given by the following relationships:

$$\begin{aligned} [\text{Cl}]_{\text{ext}} \text{ at first plateau} &= 65.8 \pm 2.8\% \\ [\text{Cl}]_{\text{ext}} \text{ at second plateau} &= 21.5 \pm 3.4\% \\ [\text{Cl}]_{\text{ext}} \text{ at third plateau} &= 10.6 \pm 2.9\% \end{aligned}$$

Since the total amount of chloride released after the first three solutions changes amounts, on average, to 97.9%, it can be seen that for some cannon a fourth electrolysis solution is required to complete the desalination.

In planning the treatment of cannon it is often useful to have an estimate of how long it will take before it is necessary to change the wash solutions. Analysis of the corrosion and washing data shows that there is a relationship between the extent of corrosion and the time it takes to reach the first and subsequent plateaus. The general form of the equation is

$$t_n = k_n / d_g \quad 4$$

where t_n is the amount of time (in days) to reach the n^{th} plateau, d_g is the annual

depth of graphitisation of the cannon (in $\text{mm} \cdot \text{y}^{-1}$) and k_n is a constant for the n^{th} plateau. The values for the plateau constants are $k_1 = 33.9 \pm 5.6$, $k_2 = 68.5 \pm 20$ and $k_3 = 103 \pm 45 \text{ days} \cdot \text{y} \cdot \text{mm}^{-1}$. The increasing standard deviations associated with the time taken to reach the subsequent plateaus is due to the natural errors associated with the variability of the depth of corrosion over the surface of the cannon and also due to the non-standard conditions associated with the electrolysis of the cannon. **All the above relationships apply to deconcreted cannon that are undergoing electrolysis in sodium hydroxide.** The chloride extraction kinetics of the *Zuytdorp* cannon did not follow the same relationships because the tompson effectively sealed the bore of the cannon².

Dating

If the date of the wreck is unknown it may be possible to use the depth of graphitisation and the chloride ion extraction rates to calculate the age of the vessel. Since the average annual depth of graphitisation d_g is obtained by dividing d by the time between sinking and recovery, t_w , equation 3 can be rearranged to give

$$d_g = \{(R+0.11)/3610\}^{1/2} = d/t_w,$$

or more simply in the form

$$t_w = 60.08 d/(R+0.11)^{1/2} \quad 4$$

The applicability of equation 4 as a dating has been used on a number of wrecks of known dates, chloride release rates and depths of graphitisation. The results are shown in table 4 where the calculated t_w dates agree with actual dates within the error range of $-3.9 \pm 4.8\%$. When consideration is given to all the variables associated with dating an object from kinetic data, the agreement is very good and promises to be of value to conservators and archaeologists.

Table 4. Comparison of calculated and real times of immersion of corroded iron cannon.

Vessel	$R \text{ mg} \cdot \text{cm}^{-2} \text{ hr}^{-1/2}$	$d \text{ mm}$	t_w years	t_{actual} years
<i>Trial</i> 3207 (1622)	7.5	17.2	375	363
<i>Batavia</i> 80309 (1629)	11.1	18.0	323	347
<i>HMS Sirius</i> 49 (1790)	67.4	25.0	183	195
<i>Rapid</i> 4032 (1811)	14.6	10.0	157	167

Composition and corrosion

The composition of eight cannon from different wreck sites dating from the seventeenth to the nineteenth century have been determined by chemical analysis of core samples taken when the connections were being made for the attachment of the cathodic current cable. The data is summarised below in table 5. In general the composition of the cannon varies remarkably little from the earliest guns of the *Trial* (1622) to the wreck of the *Rapid* (1811), with typical carbon contents of $3.66 \pm 0.7\%$.

The asterisked values in table 5 for the *Vergulde Draeck* and the *Trial* relate to a corroded sample rather than parent metal and so the carbon content is anomalously high and is not a reflection of the basic core composition. There are two sets of typical sulphur impurity levels; one set of five cannon has average values of $0.059 \pm 0.026\%$ and the other three $0.20 \pm 0.09\%$. The lower values are typical of material that was produced in a charcoal fuelled furnace⁵. There is sufficient manganese in all the cannon to form manganese sulphide inclusions and so effectively remove the sulphur from the metallurgy of the metal. Normally, higher sulphur levels tend to promote formation of coarser graphite flakes.

The amount of silicon for the *Sirius* (1790) carronade is very low at a value of $0.10 \text{ wt.}\%$ compared with the average value for four of the other cannon of $1.57 \pm 0.26\%$. Higher silicon levels promote graphite formation and suppress carbide formation; this may account in part for the extensive corrosion of the

Table 5. Composition of cast iron ordnance recovered from historic shipwrecks.

Artefact	C	S	Si	Mn	P	Ni	Cu	Cl	Carbon eq.†
<i>Rapid</i> 4032	4.0	0.18	1.93	0.475	0.37	0.22	0.023	0.005	4.8
<i>Batavia</i> 8720	4.45	0.12	1.45	0.330	0.32	0.019	0.007	1.95	5.0
<i>Cumberland</i> 52	2.90	0.075	1.57	0.275	0.30	0.013	0.016	<0.005	4.7
<i>Trial</i> 3207	9.4*	0.30	2.54	0.315	0.74	0.019	0.013	1.31	n.a.
<i>Fairy Queen</i> 3516	2.80	0.015	3.13	1.30	1.04	0.021	0.011	0.0002	4.2
<i>Vergulde</i> <i>Draeck</i> 2435	6.85*	0.070	1.33	0.76	0.40	0.012	0.006	<0.0002	n.a.
<i>Zuytdorp</i> 3926	4.30	0.055	0.80	0.115	0.46	<0.005	0.065	0.29	4.7
<i>Sirius</i> 49	3.5	0.08	0.10	0.48	0.51	0.015	0.015	0.19	3.7

* The analyses for the *Trial* and *Vergulde Draeck* cannon gave anomalously high carbon values because the metal was corroded.

† The carbon equivalent is defined by $C_{eq} = C + 1/3(Si + P)$. n.a. = values for these cannon were not calculated.

carronade. High levels of phosphorus and low levels of silicon are both associated with a low temperature of blast furnace operation¹⁵.

The *Rapid* cannon bears the cipher of G III R and so it is unmistakably an English cannon—the high nickel impurity is probably associated with a particular nickel mineral deposit that was coextracted with the iron ore. The only cannon with atypical composition is that of the *Fairy Queen* (1875); the 2.54% silicon content is very high and in a similar way the manganese level of 1.30% and 1.04% phosphorus are indicators of poor foundry practice or just a low quality ore. One of the apparent consequences of the composition is that the corroded zone of the cannon spalls away from the bulk of the object once it has been placed in alkaline solutions.

It was originally thought that drying out of the first *Fairy Queen* cannon prior to electrolysis treatment had caused the exfoliation. The second cannon of the matched pair was transported to the laboratory in a wet state and soaked in sodium hydroxide solutions without electrolysis and it too exfoliated. The small cannon have suffered from the high manganese content which favours formation of iron carbide (cementite) and the high phosphorus content would have made the metal brittle. The lower carbon content may have also contributed to the outer zone of the cannon having a different microstructure to the bulk of the material.

Conclusion

The analysis of data associated with the desalination of corroded iron cannon during soaking and electrolysis in sodium hydroxide solutions, has provided an insight into the phenomena that control the rates of the process. From the interpretation of the washing and corrosion data obtained from twenty six cannon and ten wreck sites, it has been possible to develop a series of equations and relationships. The relationship $t_n = k_n/d_g$ provides a method of calculating the number of days, t_n , it will take to reach the first and successive chloride concentration plateaus in the electrolysis solutions. The constants k_n have been experimentally determined and the annual depth of graphitisation, d_g , is the total depth of graphitisation, d , divided by the number of years of immersion. The total depth of corrosion is determined by drilling into the graphitised (corroded) metal until the drill-bit comes into contact with solid cast iron. The plateau constants and their relationship with d_g means that prediction of the treatment times is now possible.

The rate at which the chloride ions will be released is given by $R = 3610 d_g^2$

– 0.110, where R is the normalised rate of chloride ion removal, expressed in terms of $\text{mg} \cdot \text{hr}^{-1/2} \text{cm}^{-2}$. The total number of kilograms of chloride ions to be extracted in the electrolysis treatment programme is given by $\Sigma \text{Cl} = 0.0367d^2 + 2.61$. Conservators can now use these relationships to provide a guide as to how long an electrolysis treatment will take. The data also provides a monitoring device of the extent to which the conservation programme has been completed. The normalised rate of chloride ion extraction can be used to calculate the sea water immersion time for cannon when the date of the shipwreck is unknown. This provides conservators and archaeologists with an unexpected dating method since the composition of cast iron cannon would normally only provide dating to within a century or two.

Acknowledgments

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Note

1. All corrosion potentials are relative to the Normal Hydrogen Electrode (NHE) unless otherwise stated. The values have been calculated from the Ag/AgCl potentials recorded in the field.

Abstract

A new technique for removing corrosion products on lead has been developed, using electrolytic reduction followed by hydrogen plasma cleaning. The cleaned lead surface is stabilized in an oxygen plasma, which creates a thin layer of Litharge (PbO). This layer proved to be more protective than several other chemical protective coatings. Fine surface details have been preserved, even on badly corroded objects.

A New Method for Cleaning and Conservation of Lead Objects Using Hydrogen and Oxygen Plasma

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Introduction

This work was initiated by an urgent need to preserve 160 17th-century lead coins in a collection from Tranquebar, India. They had been stored in oak cabinets for about half a century. During the years, the coins have been treated in different ways and protected with different coatings, mainly paraffin wax.

A recent examination by X-ray diffraction showed that hydrocerussite (basic lead carbonate) was present on all coins and lead formate was present on a few as well. Various degrees of deterioration were found. The early stages of the attack, however, was almost invisible on many coins, but about one fourth were badly corroded and some completely destroyed. After a period of active corrosion the bulk metal had gradually turned into a white powder, held together only by the wax coating.

Experiments showed that fine surface details on the badly corroded coins were difficult to preserve when the coins were washed to remove chemicals after a consolidative electrolytic reduction. In order to clean the surface without disturbing the position of the reduced material, we tried to use hydrogen plasma treatment, considering the high reactivity of hydrogen plasma to salt traces and minerals (1).

Gas plasma reactions have been utilized for about a decade to clean and preserve antiquities. Plasma treatment of corroded objects is an attractive method compared to chemical treatment in liquids. Hydrogen and oxygen were the first gasses to be investigated in gas plasma reactions, because the properties of their plasmas were expected to be useful—atomic hydrogen is a strong reducing agent and atomic oxygen is a strong oxidizing agent (2).

Hydrogen plasma reduction has been used with success for reduction of silver tarnish on daguerrotypes, on corroded iron, silver and bronze, and on badly corroded iron meteorites and archaeological iron objects (3–8). These positive results encouraged us to investigate the possibilities of using plasma techniques for cleaning and conservation of lead, i.e., reduction of hydrocerussite and lead formate and for the formation of a protective layer of lead oxide.

Initial experiments with reduction of hydrocerussite in a hydrogen plasma showed that objects with a thin corrosion layer could be cleaned in the hydrogen plasma as the only reductive treatment. However, the reduced lead acted as a tight barrier when the reduction process had penetrated 0.1–0.2 mm into a thick corrosion layer. Some kind of pretreatment was thus required for corrosion layers exceeding 0.1–0.2 mm. For such objects, we first used an electrolytic reductive pretreatment.

The theoretical background of plasma reactions and sputtering has been described elsewhere (7–10).

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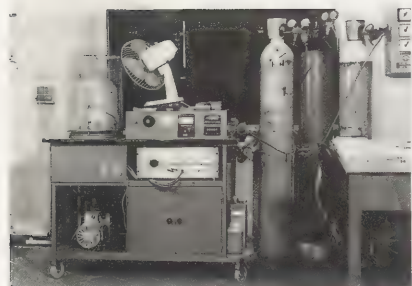


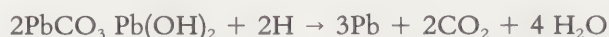
Figure 2. The home-built plasma apparatus, Model 1980, showing the belljar (left), with the faint glow from a D.C. discharge, and the right hydrogen, oxygen, and nitrogen flasks (right). Under the table are the vacuum pump, power supply and monitoring units.

The AC hydrogen plasma reduction treatment

The plasma apparatus has been described earlier in detail (8). Atomic hydrogen was created by means of an AC glow discharge in a vacuum glass belljar containing molecular hydrogen at low pressure. The plasma was continuously produced at the following parameters: discharge voltage 700 V RMS, discharge current 5 mA, and vacuum pressure 0.5 mbar. Pure hydrogen was continuously admitted to the belljar at a flowrate of 30 standard ml/min. The corroded lead objects were placed on horizontal electrodes of aluminium.

Because of the low melting point of some lead alloys, the temperature of the objects was measured with an iron-constantan thermocouple attached to either the object itself or near to the Faraday dark space. It was possible to keep the temperature below 35°C. The treatment period was one hour on each side.

The reaction between hydrocerussite and atomic hydrogen can be written as follows:



The carbonic acid and the water are gaseous under these conditions and are removed from the belljar by the continuous flow.

In the initial experiments, eight differently corroded coins were treated and the progress of the treatment was tested by means of X-ray diffraction analysis. We found that the surfaces were clean after 30–40 minutes of treatment. However, we decided on a period of treatment of one hour on each side.

A problem occurred with very porous coins containing remains of salts. These coins gave strong visible spot discharges at 700 V, contaminating the surrounding coins and electrodes with carbon (showing up as thin layers of yellow, red/blue, and brown colours). Such coins were immediately removed from the vacuum chamber to be treated separately. To avoid the spot discharges, the voltage was increased slowly to the normal operating voltage over the course of about one hour. When a voltage of 700 V had been obtained without spot discharges, the remaining treatment time was set to one hour on each side.

The AC oxygen plasma oxidation treatment

After the hydrogen plasma reduction, the newly formed lead is very reactive, and an oxide layer is created spontaneously on exposure to the atmosphere. As mentioned before, the oxide layer is vulnerable to pollutants and must be created in a clean atmosphere if it is intended to offer protection against corrosion.

To create a clean lead oxide surface, the oxidation was performed in the vacuum chamber by means of an oxygen plasma. The optimal operating conditions for the oxygen plasma were found to be: discharge voltage 450 V RMS, discharge current 10 mA, oxygen flow rate 30 standard ml/min, and vacuum pressure 0.5 mbar. The temperature on the objects was below 65°C. The treatment period was again one hour on each side.

During the first 10–15 minutes of the oxygen treatment, the colour of the lead oxide layer changed from yellow to blue, then turned colourless and transparent. This gave the coins a slightly glassy appearance. X-ray diffraction analysis showed that the surface layer created by the oxygen plasma treatment was litharge, PbO. No other lead oxide was found, and it was not possible, by changing the operating conditions, to create other oxides.

Accelerated corrosion tests

To evaluate the ability of the plasma created oxide layer to prevent corrosion, comparative corrosion tests were performed on differently treated lead samples. The samples were exposed to fumes of acetic acid and carbon dioxide (in excess) at relative humidities of 75–95% RH. The tests were carried out in a 22 l dessicator. The test samples (cut out of a commercial lead plate, 99.8 wt%) and lead coins (containing only traces of other elements) were placed on a perforated plate in the middle of the chamber.

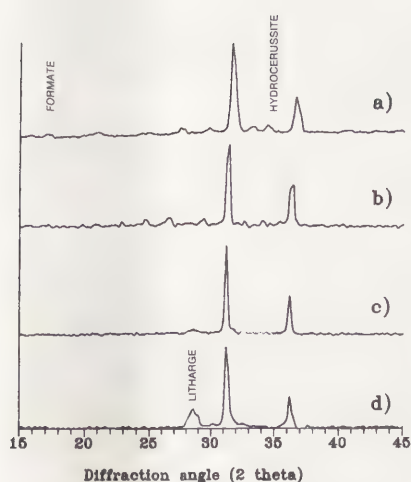


Figure 3. X-ray diffraction analysis of a lead coin. a) Before treatment: Lead, hydrocerussite, lead formate. b) After electrolytic treatment. Lead and remains of corrosion products. c) After hydrogen plasma treatment. Clean lead surface. d) After oxygen plasma treatment. Lead, litharge.



Figure 4. A coin representing the average corrosion state of the 160 treated lead coins. a) The lead coin before treatment. b) The lead coin after treatment. The appearance of the litharge layer is slightly glassy.

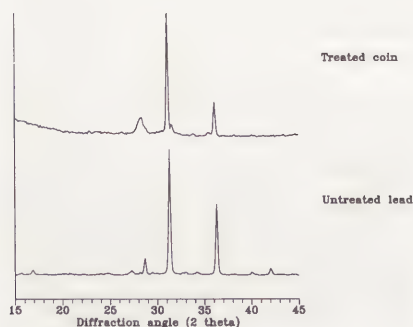


Figure 6. X-ray diffraction of oxygen plasma treated coin and untreated lead surface after six months in storage cupboard. The treated coin shows only litharge (the broad peak near 29°); on the untreated surface both lead formate and litharge are detectable. (Diffraction peaks from metallic lead are seen near 31° and 36° .)

The corrosive environment was created by pouring 4.5 ml 80 wt% acetic acid and 80 ml water supersaturated with carbon dioxide into the dessicator. The relative humidity was kept near 95% RH by means of a controlled leak.

The accelerated corrosion tests were performed on lead surfaces, treated according to methods suggested in the literature for protection of lead surfaces, as well as on oxygen plasma treated surfaces. The methods were:

- No treatment (newly polished lead).
- Naturally oxidized lead (at least 10 years old).
- Lead treated 30 seconds in diluted H_2SO_4 .
- Lead treated 30 min in diluted H_2SO_4 .
- Lead treated in $\text{K}_2\text{Cr}_2\text{O}_4 + \text{H}_2\text{SO}_4$.
- Lead treated as anode in potassium iodide electrolyte for 1 hour at 1 volt (12).

After 12 hours in the dessicator, the slightly glassy appearance of the plasma treated surfaces turned dull, and the test was stopped. Figure 4 shows the samples after the corrosion test. The protective power of the litharge layer created in the oxygen plasma, compared to the other methods, is evident from the figure. Figure 5 shows a close-up of one of the coins from Figure 4.

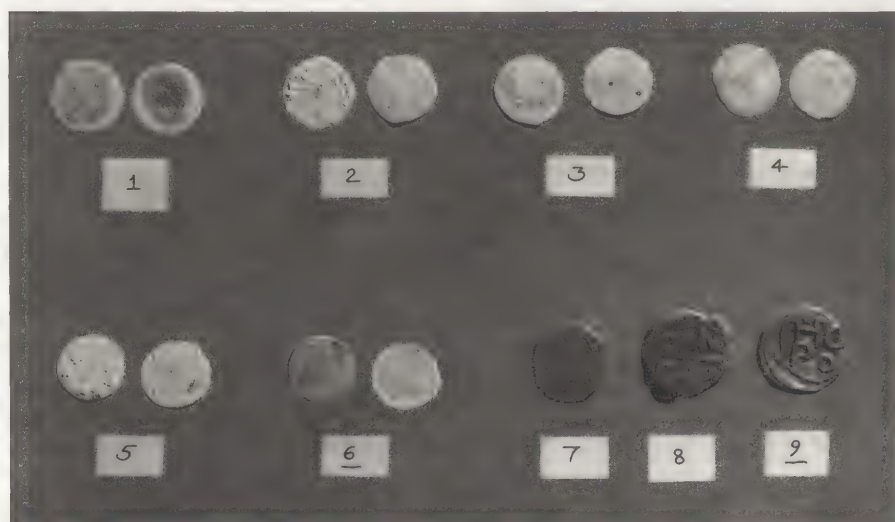


Figure 5. The result of an accelerated corrosion test after 12 hours in the corrosive atmosphere. Surface treatments are: 1) polished lead (no treatment); 2) naturally oxidized lead; 3) 30 sec in diluted H_2SO_4 ; 4) 30 min in diluted H_2SO_4 ; 5) 30 min in $\text{Cr}(\text{SO}_4)_2$; 6) 1 hour at 1 volt as anode in a potassium iodide electrolyte; and 7), 8), and 9) the 1 hour plasma oxidized coins. (Coin number 8 is the same as shown in Figure 6.)

A final corrosion test was made under more natural conditions; eight coins treated with hydrogen and oxygen plasma and eight polished lead surfaces were placed in a covered drawer from the cupboard where some of the corroded coins had been stored. After half a year spots of corrosion could be recognized on the coins under microscope. The corrosion attack on the polished surfaces was visible with the naked eye as a thin white covering. Figure 6 shows X-ray diffractograms of treated and untreated surfaces. On the polished surfaces, both lead formate and litharge had been formed, while the oxygen plasma treated surfaces only showed the litharge. (The broader diffraction peak in this case can be attributed to a much smaller crystal grain size.)

Handling precautions

The first step in the treatment procedure must be to remove earlier applied waxes or lacquers, either by solvents or in a hydrogen or oxygen plasma. After hydrogen plasma reduction the surface layers appear dull in hue. However, as the thin reduced layer is very soft, just a light pressure (e.g., from the weight of the object itself) makes the touched area shining metallic lead gray.

The outmost cleanliness must be observed after the hydrogen plasma treatment in order to avoid contamination of the surfaces. For the same reason, delay

between hydrogen plasma treatment, oxygen plasma treatment, and a recommended final protective organic coating must be minimized.

Application of an organic coating (paraffin wax) on the newly created oxide layer is advisable, if loosely adherent material is to be kept *in situ*.

Conclusion

We have developed a new method for cleaning and corrosion protection of lead objects using hydrogen plasma and oxygen plasma, respectively. The method has four main steps: electrolytic reductive pretreatment (when thicker corrosion layers are present), hydrogen plasma cleaning/reduction, litharge layer creation in an oxygen plasma, and a final protective organic coating.

Accelerated corrosion tests have shown that the litharge layer created in the oxygen plasma is a more efficient surface protector on lead than other chemical surface protecting layers and naturally created surface oxides. However, the plasma treatment alone can not entirely prevent recorrosion.

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Abstract

In the United States, a number of techniques have been used to remove corrosion from outdoor bronze sculptures. Most employ particulate abrasives. This study compares the two methods, bronze wool and walnut shells, in common use with the application of medium pressure water 13.8–27.6 MPa (2000–4000 psi). Medium pressure water produces controlled erosion that removes soluble corrosion products at the surface of the bronze. Tests were performed *in situ* on weathered sculptures and documented by photomicroscopy and X-ray diffraction of pre- and post-treatment surfaces.

Keywords

Bronze, sculpture, corrosion, cleaning, walnut shells, bronze wool, medium pressure water, conservation, photomicroscopy, X-ray diffraction

Field Tests on Removing Corrosion from Outdoor Bronze Sculptures Using Medium Pressure Water

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Introduction

This investigation of corrosion removal using medium pressure water (mpw) on outdoor bronze sculptures developed from the treatment of a 19th-century monument located in Washington, DC (1). The importance and location of the sculpture led the senior author to seek an effective means of corrosion removal that also offered a qualitatively different patina with a wider than usual range of color. The relationship between patina and mpw has been discussed elsewhere (2). Extremely high vehicular traffic made it desirable to use a process that did not create hazardous dust. The use of mpw was explored as a way to meet these objectives. Tests were conducted to verify and document its effectiveness.

This paper compares corrosion removal by fine grade bronze wool, walnut shells, and mpw. Walnut shells and bronze wool were selected for comparison with mpw because they are commonly used in conservation practice. All tests were performed on sculptures *in situ*.

Rationale for use of medium pressure water

Corrosion removal from outdoor bronzes reflects an evolution in the selection of materials over the past few decades. The conservation field has searched for effective materials that are less and less damaging to the bronze sculpture. Sand, glass or plastic beads, and organic materials such as walnut shells have all been employed. Independent of the medium used, abrasive techniques have certain inherent limitations. If the abrasive is harder than the bronze substrate, corrosion and bronze metal are removed. If the abrasive is softer, loose corrosion is removed, but remaining corrosion products may be compressed. The relatively large size of abrasive media with respect to corrosion pits prevents the physical removal of deleterious corrosion from the pits.

The corrosion that forms on outdoor bronzes is largely a result of the pH and pollutants of the surrounding environment (3). Copper sulfates, nitrates, and chlorides form the most deleterious corrosion products because they are made more soluble, reactivating the corrosion, with each acidic rain or snowfall. This creates damaging corrosion cells (4).

The application of water under pressure offers a potential for improved corrosion removal. The effectiveness of water results from the mechanical removal of surface corrosion, which is then flushed from the surface and corrosion pits. Lins recently documented that the use of water, even ultra high pressure (uhp) water-jet blasting 240 MPa (35,000 psi), did not deform or harden bronze substrates; however, uhp can produce microtunneling with resulting metal loss (5). Medium pressure water 13.8–27.6 MPa (2000–4000 psi) avoids the microtunneling associated with the uhp range.

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Objectives

The comparison of medium pressure water to walnut shells and bronze wool during the field tests had two primary objectives. The first was to determine if mpw would remove the same amount of corrosion as walnut shells or bronze wool. The second was to identify important variables of mpw and to establish their relationship to the amount of corrosion removed. For these field tests, the desired degree of corrosion removal was defined as surface corrosion removed from the pits and no bright metal visible at $15\times$ magnification.

The mpw method needed to meet several additional criteria: to provide a work environment that limited dust, eliminate accumulation of debris, and use affordable, readily available equipment.

Test site selection

Tests were conducted in the field on outdoor bronzes and reflect the typical inconsistencies and corrosion variables of aged castings. Tests were performed in unobtrusive locations, typically on the top of the sculpture's self-base. Tested sculptures included the range of surface appearances generally seen on historic sculptures. The following sculptures were tested:

1. "Garfield Memorial," Washington, DC; sculptor, J.Q.A. Ward. Henry Bonnard Foundry, 1888. Predominantly light green.
2. "Columbus," St. Paul, Minnesota; sculptor, Charles Brioschi. Roman Bronze Works, 1931. Light green color with black in the recesses; streaked.
3. "Knute Nelson," St. Paul, Minnesota; sculptor, John Daniels. Roman Bronze Works, 1928. Predominantly black surface color; heavy pitting, with light green on the shoulders and head.

Test methods

Comparative tests of corrosion removal were conducted using mpw, air abrasion with walnut shells, and rubbing with bronze wool. The bronze wool and walnut shell tests were performed with techniques commonly used by conservators (6). While the three methods are based on different principles, comparison of the corrosion removed provides a useful departure point. Variables included in the tests are detailed in Table I.

Available rental equipment and the limitations associated with treating life-size sculpture in part defined the test variables. Most rental equipment companies have pressure washers providing up to 27.6 MPa (4000 psi). The vendors stated that higher pressure machines are not commonly available for rent due to their high cost and the usual abuse of rental equipment; in addition, some cities and unions regulate the use of heavy industrial equipment.

Two conservators performed the tests; there was no noticeable operator variance (7). Test techniques and variables were as follows:

1. Corroded surfaces were rubbed with fine grade bronze wool using both horizontal (side-to-side) and circular motions.
2. Grade AD 10.5-B (60/200 mesh) walnut shells were applied through 7.94-mm and 9.52-mm nozzles at 240 KPa (5/16 in and 3/8 in nozzles at 35 psi) (regulated at the abrasive container). Multiple horizontal or vertical passes were made while maintaining the nozzle perpendicular to the surface or at an angle 0.262 rad (15°) off perpendicular. Durations of 1 and 4 seconds per 650 mm^2 (in^2) were used.
3. City water was propelled cold through a 0.436 rad (25°) nozzle at pressures ranging from 6.9 to 27.6 MPa (1000 to 4000 psi). Mpw tests were performed sequentially from lower to higher pressures. Nozzle angle ranged from perpendicular to the surface (0 rad or 0°) to an angle 1.047 rad (60°) off perpendicular. The working distance was 200 mm (8 in). Multiple passes were made with the major axis spray pattern aligned to the edge of the self-base transversely or longitudinally (See figs. 1, 2).

The variable being tested determined the size of the test site and reflected a minimum size consistent with normal motion and application of the technique.

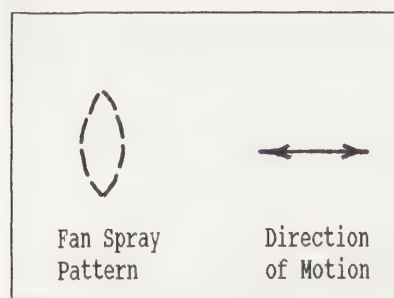


Figure 1. Transverse Motion.

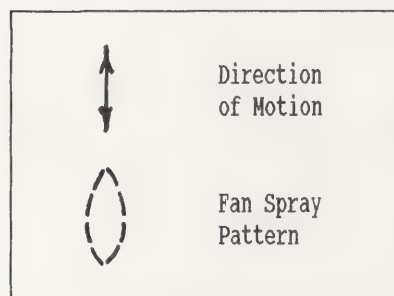


Figure 2. Longitudinal Motion.

Table I. Methods and variables tested.

Test	Method	Pressure MPa (PSI)	Rate mm ² /s (sec/in ²)	Working distance mm (in)	Nozzle	Angle rad (°)	Motion*
#1	Control						
#2	Bronze wool		130 (5)				H C
#3	Bronze wool		65 (10)				H C
#4	Walnut shells	0.240 (35)	650 (1)	150 (6)	9.52 mm (3/8 in)	0.262 (15)	H
#5	Walnut shells	0.240 (35)	160 (4)	150 (6)	9.52 mm (3/8 in)	0.262 (15)	H
#6	Walnut shells	0.240 (35)	650 (1)	200 (8)	7.94 mm (5/16 in)	0 (0)	H V
#7	Walnut shells	0.240 (35)	160 (4)	200 (8)	7.94 mm (5/16 in)	0 (0)	H V
#8	Water pressure	6.9 (1000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	T
#9	Water pressure	13.8 (2000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	T
#10	Water pressure	20.7 (3000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	T
#11	Water pressure	27.6 (4000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	T
#12	Water pressure (on top of site for test #5)	27.6 (4000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	T
#13	Water pressure	13.8 (2000)	260 (2.5)	200 (8)	0.436 rad (25°)	0 (0)	L
#14	Water pressure	13.8 (2000)	130 (5)	200 (8)	0.436 rad (25°)	0 (0)	L
#15	Water pressure	13.8 (2000)	65 (10)	200 (8)	0.436 rad (25°)	0 (0)	L
#16	Water pressure	13.8 (2000)	43 (15)	200 (8)	0.436 rad (25°)	0 (0)	L
#17	Water pressure	13.8 (2000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	L
#18	Water pressure	27.6 (4000)	260 (2.5)	200 (8)	0.436 rad (25°)	0 (0)	L
#19	Water pressure	27.6 (4000)	130 (5)	200 (8)	0.436 rad (25°)	0 (0)	L
#20	Water pressure	27.6 (4000)	65 (10)	200 (8)	0.436 rad (25°)	0 (0)	L
#21	Water pressure	27.6 (4000)	43 (15)	200 (8)	0.436 rad (25°)	0 (0)	L
#22	Water pressure	27.6 (4000)	32 (20)	200 (8)	0.436 rad (25°)	0 (0)	L
#23	Water pressure	27.6 (4000)	22 (30)	200 (8)	0.436 rad (25°)	0 (0)	L
#24	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	0 (0)	L
#25	Water pressure	27.6 (4000)	13 (50)	200 (8)	0.436 rad (25°)	0 (0)	L
#26	Water pressure	27.6 (4000)	11 (60)	200 (8)	0.436 rad (25°)	0 (0)	L
#27	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	0 (0)	L
#28	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	0.262 (15)	L
#29	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	0.524 (30)	L
#30	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	0.787 (45)	L
#31	Water pressure	27.6 (4000)	16 (40)	200 (8)	0.436 rad (25°)	1.047 (60)	L

* H = horizontal; C = circular; V = vertical; L = longitudinal; T = transverse.

For example, approximately 150 × 200-mm (6 × 10 in) areas were used to evaluate the surface appearance produced by mpw with different nozzles at different working distances. To test the effect of changing water pressure when other variables were held constant, approximately 50 × 100-mm (2 × 4 in) areas were treated. Test areas for the effect of changes in mpw variables were 25 × 25 mm (1 × 1 in), with neighboring surfaces masked to allow broadpasses typical of treatment of a life-size sculpture.

Tests were documented using written descriptions of observations together with "before" and "after" photographs. Photomicroscopy was used instead of the more commonly employed macrophotography to enable documentation of the extent of corrosion removal. An Olympus SZ-60 stereo-zoom microscope was used to view surfaces at 10× to 95× magnification (8). A magnification of 15× was selected as most informative for the comparative purposes of this study.

Results and discussion

Table I lists 31 tests by method and variable. Variables are inter-related; that is, changing one element generally necessitates adjustment of one or more additional variables to produce comparable corrosion removal. Ultimately, a change in any variable in Table I affects the amount of corrosion removed or the character of the surface that remains.

Test 1. This area was left untreated to serve as a reference (See fig. 3).

Tests 2–3. Since bronze wool is the same metal as a bronze sculpture, in theory, it should have the same hardness on the Mohs scale, and not abrade the sculpture.



Figure 3. Test #1. Control.

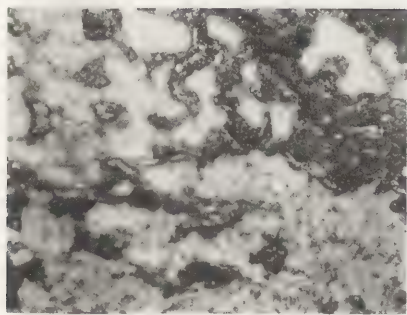


Figure 4. Test #2 after Bronze Wool Treatment.

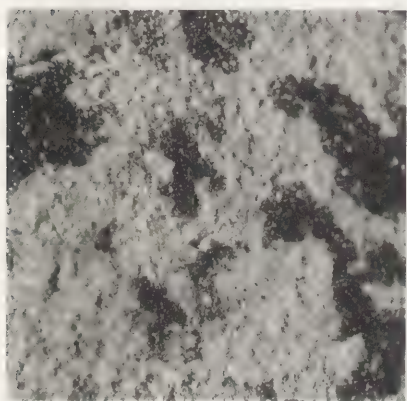


Figure 5. Test #6 after Walnut Shell Treatment.

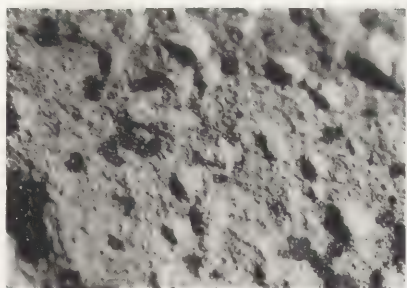


Figure 6. Test #12 after Medium Pressure Water Treatment.

The degree of corrosion removal and the effect on the sculptures were documented.

In this study corrosion removed by fine grade bronze wool appeared approximately equivalent to that removed using walnut shells. Photomicrographs revealed that bronze wool abraded the higher or upper surfaces of the bronze when the surface was rough or pitted. The bronze was scratched, revealing bright metal, and corrosion remained in the pits. Although easily seen at $15\times$ magnification, these scratches are barely visible with the unaided eye (See fig. 4). Bronze wool requires more time than either the walnut shells or medium pressure water methods.

Tests 4–12. Because the relationship of variables in walnut shell treatments has been well documented, they were not explored further in this study (9). Settings used in these field tests were within the range commonly used in sculpture conservation in the United States.

Removal of corrosion with walnut shells was found to be approximately equivalent to that achieved using mpw between 6.9 MPa and 13.8 MPa, 32 mm²/s transverse motion, 0.262 rad nozzle (1000 and 2000 psi, 20 mm²/s [sec/in²]) transverse motion, 25° nozzle perpendicular to the surface at an 200-mm (8 in) working distance. Examination of surfaces under 15x magnification showed that only corrosion higher than the black pollution deposits was removed (See fig. 5).

Tests 8–12. This series demonstrated that the rate of removal increased with increasing water pressure. In comparison with the other techniques tested, 27.6 MPa (4000 psi) was found to remove the greatest quantity of corrosion without visible damage to the bronze. Evidence of original patinas could be seen in recessed areas of the sculpture after mpw treatment, as with the walnut shell technique. To eliminate the question of site variability, 27.6 MPa (4000 psi) mpw was applied to test site #5, where walnut shells had previously been used. Additional corrosion was removed with mpw, including removal of corrosion from the underlying pitted surface (See fig. 6).

Tests 11, 22, 24. These tests compared the effect of major axis alignment of the water fan and the rate in mm²/s (sec/in²) on corrosion removal.

In these test sites, the fan major axis aligned transversely (site 11) removed approximately twice as much green surface corrosion as with the axis aligned longitudinally (test 22). When the rate was increased (site 24), the same amount of corrosion could be removed (as in site 11).

Tests 13–22. The variable rate sequences at 13.8 MPa and 27.6 MPa (2000 psi and 4000 psi) sought to establish whether lower water pressure could remove the same amount of corrosion as higher pressure if duration of application was increased.

The corrosion removed in test 16 of 13.8 MPa for 43 mm²/s (2000 psi for 15 sec/in²) with longitudinal motion was equivalent to that removed in test 18 of 27.6 MPa for 260 mm²/s (4000 psi for 2.5 sec/in²) with longitudinal motion, thereby documenting such a relationship. Given the size of a typical outdoor sculpture, it would take approximately six times longer to remove equivalent corrosion at 13.8 MPa (2000 psi) as at 27.6 MPa (4000 psi). Use of 27.6 MPa (4000 psi) is significantly more time efficient.

Tests 23–26. This sequence of increasing rates at 27.6 MPa (4000 psi) explored how much corrosion could be removed with mpw. Although unaided visual examination of the surface after 50 and 60 seconds of mpw showed only a darkened green color, microscopic examination of the sites revealed spots of bright metal.

Tests 27–31. The angle of the nozzle with respect to the surface during corrosion removal was studied to determine the most effective angle for the 27.6 MPa (4000 psi) setting.

In contrast to water cleaning at pressures less than 13.8 MPa (2000 psi), which are more effective at ± 0.524 rad ($\pm 30^\circ$) off perpendicular, mpw corrosion removal is more effective at 0 rad or 0° angle (perpendicular to the surface).

X-ray diffraction (XRD) analysis

Initial work has been completed using XRD to determine the corrosion products present prior to any corrosion removal, corrosion products remaining after treatment with walnut shells, and corrosion products remaining after use of the mpw technique. Samples were taken using acetate tape, leaving the underlying cuprite layer intact. Diffraction peaks were identified as copper sulfate hydroxide (Brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$, JCPDS #13-398). Sample 24 contains the highest concentration of the phase, followed by sample 25 and then sample 19 (10). Sample 19 did not contain sufficient brochantite for detection by the diffractometer. Results are summarized in Table II.

Table II. XRD analysis tests.

Test site	Corrosion removal method	XRD sample	Results
#1	None	#24	Highest concentration of brochantite present.
#6	Walnut shells	#25	Brochantite present with a lower concentration than #1.
#11	Medium pressure water @ 27,6 MPa, 32 mm ² /s (4000 psi, 20 sec/in ²), trans. motion	#19	No brochantite detectable.

Conclusions

The two corrosion removal methods, bronze wool and walnut shells, commonly used by conservators in the United States were compared with the medium pressure water method in a series of field tests to evaluate the relative efficacy of the techniques. Bronze wool was shown to abrade the surface of historic bronzes, producing bright scratches and leaving corrosion in the corrosion pits. It was observed that after treatment with walnut shells, substantial corrosion remained on lower surface levels, the eroded surfaces that result from corrosive action over time. This was especially evident in the corrosion pits. X-ray diffraction analysis confirmed that brochantite was reduced, but still present. The amount of corrosion removed with walnut shells can be approximated with mpw between 6.9 MPa and 13.8 MPa at 32 mm²/s (1000 and 2000 psi, 20 sec/in²) with transverse motion, 0.436 rad (25°) nozzle perpendicular to the surface, and a 200-mm (8 in) working distance.

Tests demonstrated that more corrosion could be removed with the medium pressure water technique than with the walnut shell or bronze wool techniques. The tests showed progressively more corrosion was removed as pressure and time were increased. The amount of corrosion removed can be controlled by changing one or more variables (pressure, rate, nozzle, working distance, angle, and fan axis alignment). Good judgement on the part of the operator remains essential to the safe and effective execution of this technique, since mpw can be tailored to remove a desired amount of surface corrosion.

Microscopic examination of test sites treated with mpw at 27.6 MPa (4000 psi) showed changes in color and surface texture with no deleterious effects visible. The XRD analysis showed that the potentially active, soluble surface brochantite was removed. Equipment settings for corrosion removal in these tests were 27.6 MPa (4000 psi) using a 252·10⁻⁶ m³/s (4 gallon per minute [gpm]) machine at a rate of 32 mm²/s (20 sec/in²) with the fan major axis aligned transversely, using a 0.436 rad (25°) nozzle perpendicular to the surface at a 200-mm (8 in) working distance.

The advantages of mpw are several; it removes soluble surface corrosion products, provides pressure sufficiently low to avoid microtunneling of the metal, avoids introducing potentially hundreds of pounds of abrasive debris into the environment, keeps the work environment free of hazardous dust problems, and can lower costs through reductions of time and materials needed to complete the work.

For the future, several areas of additional research are anticipated. The extent of corrosion product removal required to assure the preservation of an outdoor bronze sculpture remains to be resolved. Bronze cross-sections should be examined to determine the amount of active corrosion removed from pits and at the cuprite-bronze interface. Testing is needed to determine when it is appropriate to use medium pressure water, walnut shells, or bronze wool in other situations such as with corroded, painted metal sculptures or smooth modern sculpture.

Acknowledgements

We would like to thank Mr. George White, Architect of the U.S. Capitol, Dr. Barbara Wolanin, Curator of the U.S. Capitol, and Ms. Carolyn Kompelien, Site Manager of the Minnesota State Capitol Historic Site, for their interest and permission to investigate mpw corrosion removal on sculptures under their custodianship. Andrew Lins shared with us his insights, which focused the direction of our field tests. Phillip Hutchens, Chief Photographer, Minnesota Historical Society assisted us in solving the on-site photomicroscopy challenge. Ken Kilby, Leeds Precision Instruments, Minneapolis, generously provided the trinocular microscope used for this study. The reviewers of this paper—Arthur Beale, Terry Drayman-Weisser, Henry Lie, and Andrew Lins—shared many valuable suggestions which have been incorporated. Karen Motylewski provided valuable editorial assistance.

Notes

1. Water Jet Technology Association, *Recommended Practices for Use of Manually Operated High Pressure Water Jetting Equipment*, 1993 edition in press. Pressure cleaning generally refers to machines under 35.5 MPa (5000 psi), high pressure cleaning refers to 35.5–207 MPa (5,000–30,000 psi), and ultra-high pressure cleaning above 207 MPa (30,000 psi). Terminology within the industry varies. For our field tests, the focus was the medium pressure water in the range of 13.8–27.6 MPa (2000–4000 psi). We did not focus on the low pressure range, below 13.8 MPa (2000 psi).
2. Linda Merk-Gould and Barbara Wolanin, "Aesthetics, Preservation and History: The Garfield Monument," *Sculpture Conservation Symposium, United Kingdom Institute*, London, September 6, 1993. Submitted for publication.
3. Marcel Pourbaix, "Electrochemical Corrosion and Reduction," *Symposium on Corrosion and Metal Artifacts* (Washington D.C.: National Bureau of Standards, 1977), 1–16.
4. Andrew Lins (June, July, November 1992), private communications.
5. Andrew Lins, "The Cleaning of Weathered Bronze Monuments: A Review and Comparison of Current Corrosion Removal Techniques," *DIALOGUE/89-The Conservation of Bronze Sculpture in the Outdoor Environment: A Dialogue Among Conservators, Curators, Environmental Scientists and Corrosion Engineers* (Houston: NACE, 1992), 209–230.
6. The air-abrasive walnut shell method was based on conversations with practicing conservators who regularly employ the method: Mayda Jensen, Jensen Conservation Services, Omaha, NE; Henry Lie, Harvard University Art Museums, Cambridge, MA; Kent Severson, Daedalus Inc., Boston, MA; Nicolas Veloz, National Park Service, Alexandria, VA; and Cameron Wilson, Fine Objects Conservation, Inc., Westport, CT. The settings used varied within the following ranges: Grade AD 10.5B (60/200 mesh) with one group using AD 9B (30/100 mesh); 200–450 KPa (30–65 psi) but generally in the 200–240 KPa (30–35 psi) range; 9.52 or 7.94 mm (3/8 in or 5/16 in) (one group using 3.20 and 6.35 mm [1/8 in and 1/4 in]) nozzles; 150–200 mm (6 in–10 in) working distance with most at 200 mm (8 in); 0.262 rad (15°) angle or perpendicular 0 rad (0°) to the surface; 1–4 seconds per mm² (in²) but generally at 1 second (with one group at 1/4 second). All conservators use an abrasive container similar to a Lindsay 35. The selection of a compressor was based on having sufficient volumetric flow rate of m³/s (cfm) for a given pressure (psi) and nozzle size. The compressors ranged from an 8HP Emglo rated at 6.6·10⁻³ m³/s, 0.240 MPa, 3.20-mm nozzle (14 cfm, 35 psi, 1/8 in nozzle) to Sullair 100 rated at 47.2·10⁻³ m³/s, 0.240 MPa, 9.52 or 7.94-mm nozzle (100 cfm, 35 psi, 3/8 in or 5/16 in nozzle). In general, the larger compressors are used.
7. The tests on the self-base of the Columbus Statue were performed by Cameron Wilson of Fine Objects Conservation with the test selection by Mr. Robert Herskovitz (Head, Conservation Department, Minnesota Historical Society), Mr. Paul Storch (Objects Conservator for the Minnesota Historical Society), and members of the Capitol Advisory Committee for Ms. Carolyn Kompelien, Site Manager of the Minnesota State Capitol Historic Site. The tests on the self-base of the Nelson Statue

- were performed by Linda Merk-Gould of Fine Objects Conservation with the test selection by Mr. Herskovitz. In both tests, the pressure washer used was a Simpson 4040 $252 \cdot 10^{-6} \text{ m}^3/\text{s}$ (4 gpm) pressure washer, model 904 nozzle manufactured by Spraying Systems and a CatPump pressure gauge to regulate the pressure.
8. The microscope used was an Olympus SZ-6045 TRPT using illumination from a Scholly 150H Universal bifurcated fiber optic, tungsten filament light source. Visual examination was accomplished using $10\times$ eyepieces, with the zoom of the objective ranging from $1\times$ to $6.3\times$. A $1.5\times$ auxiliary lens was also employed. Photomicrographs were taken using a Nikon F3 camera body, Olympus $2.5\times$ photo eyepiece and Kodak EPJ 320T slide film.
 9. W.T. Chase and Nicolas F. Veloz, "Some Considerations in Surface Treatment of Outdoor Metal Sculptures" (Paper delivered at the Triennial Meeting of the International Council of Museums Committee for Conservation, Washington, DC, May 22-26, 1985), 23-25.
 10. Scott Schlorholtz, (October 1992), XRD Analysis Report No. 1863, Materials Analysis and Research Laboratory, Iowa State University, Ames, IO. The x-ray diffraction analysis was performed on a Siemens D-500 x-ray diffractometer with the copper x-ray tube operated at 50 KV and 25 mA in a fully computer controlled, step scan mode.

Résumé

Les auteurs présentent les résultats d'essais effectués sur des vernis et des cires utilisés sur des métaux dans le but d'obtenir une protection des surfaces contre la corrosion. Diverses techniques de vieillissement artificiel ont été utilisées sur un ensemble de 24 vernis déposés sur 4 types de métaux: cuivre, argent, fer et plomb. Des résultats intéressants se dégagent de ces essais en particulier la possibilité d'utiliser des couches multiples.

Mots clés

Métal, vieillissement artificiel, protection, vernis, conservation

Essais comparatifs de revêtements protecteurs utilisés en conservation et restauration des métaux

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Introduction

Une première série d'essais sur les revêtements communément utilisés sur les objets métalliques a été réalisée en 1984 à Draguignan (1). Elle portait sur les produits employés sur le fer et le cuivre. Depuis d'autres essais ont été menés avec les mêmes produits sur des échantillons en argent et en plomb. Récemment, les études ont été reprises sur des échantillons de fer et de cuivre pour tester une nouvelle série de produits (2,3). Enfin nous avons commencé des études qui portent sur le comportement de couches successives de vernis et de cire minérale blanche ou de paraffine.

Le but de cette étude est de rechercher les revêtements protecteurs les mieux adaptés aux supports sur lesquels ils sont appliqués en fonction de l'environnement dans lequel ils seront conservés ultérieurement (réserves, vitrines, bord de mer, ville polluée etc. . .). Une nouvelle fois ce sont des échantillons modernes qui ont été utilisés pour éviter de réaliser des tests dangereux sur du matériel rare.

La question qui peut se poser est, bien entendu, de savoir si ces essais sont représentatifs et s'ils peuvent s'appliquer à des objets anciens. S'il est impossible de se prononcer pour tous les revêtements protecteurs, nous avons cependant, avec le recul, un certain nombre de points de comparaison. C'est le cas pour les cires (4,5), les paraffines, les acétates de polyvinyles, les paraloïds (6) et certains vernis qui, maintenant, ne sont plus commercialisés comme par exemple le sicomet. Dans la totalité des cas les reprises de corrosion sur des objets précédemment traités et l'évolution des vernis nous amène à penser que les tests sont représentatifs des réactions habituelles des revêtements protecteurs.

Cette impression a d'ailleurs été confirmée par le vieillissement naturel de quelques échantillons laissés dans une boîte en plastique, à l'abri de la lumière pendant cinq ans. Les conclusions tirées des essais sont confirmées par le développement de certaines corrosions et le jaunissement de certains vernis ou des cires. Par exemple, on a pu constater une corrosion sur des éprouvettes en argent enduites de cire animale jaune ainsi que des corrosions sur des fers revêtus de Paraloïd B72.

Protocole d'essais

Les tests de vieillissement artificiel ont été conduits à partir des enceintes qui sont en service à Draguignan à savoir:

- Etuve à chocs thermiques
- Etuve à brouillard salin
- Etuve à gaz sulfureux
- Etuve à gaz carbonique
- Etuve à ultraviolets

Quand elles existent, se sont les normes AFNOR en vigueur pour les tests des vernis et des peintures qui ont été utilisées (7).

Chaque échantillon a été nettoyé mécaniquement par sablage à 20 cm avec une poudre de billes de verre calibrées de 4 à 45 microns sous une pression de 3 Kg m² à l'exception de l'argent qui a été nettoyé avec un produit commercial (argenteil). Tous les échantillons ont été ensuite dégraissés sous ultrasons avec de l'acétone avant d'être revêtus.

Deux types d'imprégnation ont été effectuées: soit par simple trempage à la

pression atmosphérique normale soit sous vide (pour une petite partie des éprouvettes). Les produits utilisés l'ont toujours été en solution à 10% dans un solvant organique (8).

L'épaisseur des revêtements déposés (Tableau n°1) a été mesurée à l'aide d'une sonde à courant de Foucault (Dermatron D8 Engelhart Industry) (a).

Tableau n° 1. Epaisseur moyenne des revêtements sur les échantillons (microns) (PN = Pression normale; SV = sous vide).

Produits	Fer		Cuivre		Argent	Plomb
	PN	SV	PN	SV	PN	PN
Synocryll	12	13	12	14	18	20
Paraloïd B48N	19	16	36	8	7	15
Paraloïd B72	15		15	8	23	25
Incalac	4		7		6	10
Pentarol 100	20		13		9	18
Rhodopas M	15	5	12	3	15	20
Blackor	9		3			
Sicomet brillant	12	10	15	15	7	10
Sicomet mat	15		5		3	8
Tetenal	15					
Paraffine	10	0	7	0	15	21
Cire Miné. Blanc.	4	0	6	7	9	19
Cire animale jau.	10	0	14	5	25	30
Cire microcrist.	35	12	6	1	17	21
Noverox	25	40				
CE 1170	54		33		40	36
Vinamul	65		60			
Plexigum N80	22		5			
Plexigum 380	9		8			
Plexigum 74	55		52			
Plexigum 75	6		10			
Plexigum 5484	2		9			
Pioloform BL	10		12			
Pioloform BM	18		10			
Paraloïd B48N + Paraffine	87		23			
Paraloïd B48N + Cire Miné. Blanc			28			
Paraloïd B72 + Paraffine			15			
Paraloïd B72 + Cire Miné. Blanc			20			
Incalac + Cire Miné. Blanc	76		43			
Incalac + Paraffine	83		23			
Rhodopas + Cire Miné. Blanc	95		40			
Rhodopas + Paraffine	82		35			
Sicomet brillant + Cire Miné. Blanc	93		30			
Sicomet brillant + Paraffine	85		17			
Synocryll + Cire Miné. Blanc	87		29			
Synocryll + Paraffine	83		21			

Les essais effectués sont les suivants:

- Chocs thermiques (CT):

En l'absence de norme adaptée, les éprouvettes sont exposées à des températures qui varient de -35°C à +100°C en 60mn puis de +100°C à -35°C dans le même

temps. Ce cycle est répété 100 fois sans intervenir sur l'humidité relative qui varie donc constamment dans l'enceinte.

– Brouillard salin (BS):

Les essais sont effectués selon la norme AFNOR X 41-002. Les échantillons sont mis en présence d'un brouillard d'eau salée (5% de Na Cl dans de l'eau distillée) maintenu constamment à 35°C pendant 144 heures.

– Etuve à gaz sulfureux (SO₂):

Les échantillons sont mis en présence de gaz sulfureux dans une enceinte fermée, saturée en humidité et portée à une température de 45°C pendant 144 heures, selon la norme AFNOR T 30-055.

– Etuve à gaz carbonique (CO₂):

En l'absence de norme adaptée, les échantillons sont exposés à une atmosphère chargée à 5% de gaz carbonique à une température de 37°C + ou - 0,5°C en atmosphère humide pendant 332 heures.

– Etuve à ultraviolet (UV):

Les échantillons sont exposés à quatre lampes UV selon la norme AFNOR T 30-049, pendant 144 heures à une température de 60°C.

Cependant il semble que les essais aient été perturbés par l'absence d'un préfiltre entre les échantillons et les lampes.

Les éprouvettes ainsi testées sont ensuite examinées pour déterminer leur degré de corrosion. Pour cela on applique sur l'échantillon un cadre dessiné sur un verre et divisé en 100 parties égales. Le pourcentage de corrosion s'obtient en comptant le nombre des carrés corrodés et ceux non corrodés. On considère que le moindre point d'altération apparaissant dans un carré fait que ce dernier est considéré comme entièrement corrodé.

A côté de cette mesure on compare également l'aspect de départ à l'aspect final (notion subjective d'esthétique). (Tableau 2).

Produits testés:

Se sont ceux utilisés par la plupart des conservateurs et restaurateurs français (b). Ils sont théoriquement réversibles. On peut les classer en cinq catégories: les acétates de polyvinyle, les butyrales de polyvinyle, les cérides, les paraffines et les acryliques. Pour certains produits commerciaux "anti-rouille" il n'a pas été possible de connaître la composition exacte.

NOM DU PRODUIT	TYPE
Blackor	?
CE 1170	Acrylique
Cire animale jaune	Céride
Cire minérale blanche	Céride
Cire microcristalline	Céride
Incalac	Acrylique
Noverox	?
Paraffine	Paraffine
Paraloïd B 48N	Acrylique
Paraloïd B 72	Acrylique
Pentarol 100	Acrylique
Pioloform BL80	Acétate de butyrale
Pioloform BM 80	Acétate de butyrale
Plexigum N80	Acrylique
Plexigum 74	Acrylique
Plexigum 75	Acrylique
Plexigum 380	Acrylique
Plexigum 5484	Acrylique

Rhodopas M
Sicomet mat
Sicomet brillant
Synocryll
Tetenal
Vinamul

Acétate de polyvinyle
Acrylique
Acrylique
Acrylique
Acrylique
Acétate de polyvinyle

Tableau n° 2. Aspect des surfaces après vieillissement. 1 = très bon; 2 = bon; 3 = moyen; 4 = mauvais; 5 = très mauvais (Pression normale). 1' = très bon; 2' = bon; 3' = moyen; 4' = mauvais; 5' = très mauvais (Sous vide).

Produit	Fer					Cuivre				
	CT	BS	UV	CO2	SO2	CT	BS	UV	CO2	SO2
Synocryll	4	4	1	2	5	1	4	2	3	5
Synocryll	1'	5'	5'			1'	4'	5'		
Paraloïd B48N	4	2	4	2	2	4	5	4	3	2
Paraloïd B48N	1'	4'	3'			1'	5'	5'		
Paraloïd B72	4	5	2	1	5	4	5	2	3	3
Paraloïd B72	1'	5'	5'			1'	5'	5'		
Incralac	4.	4	1	3	4	4	4	2	3	5
Pentarol 1000	4	4	5	3	4	4	5	4	3	5
Rhodopas M	2	5	2	1	5	4	1	2	4	5
Rhodopas M	4'	5'	4'			1'	5'	4'		
Blackor	5	5	4	4	5	4	5	2	3	5
Sicomet bril.	4	4	1	2	2	4	5	2	3	3
Sicomet bril.	1'	4'	5'			1'	5'	5'		
Sicomet mat	1	5	1	4	5	2	5	2	2	5
Tetenal	5	5	5	5	5					
Paraffine	4	4	1	4	4	4	5	1	3	5
Paraffine	1'	5'	2'			1'	5'	4'		
Cire Min. Bl	2	4	1	4	5	4	5	2	3	5
Cire Min. Bl	1'	5'	1'			1'	5'	4'		
Cire jaune	4	4	4	4	3	5	5	4	3	5
Cire jaune	1'	5'	4'			4'	5'	5'		
Cire Microcr.	3	5	1	5	5	2	5	3	4	5
Cire Microcr.	1'	5'	2'			3'	4'	5'		
Noverox	1	5	5	4	4					
CE 1170	4	5	4	4	2	2	2	1	2	3
Vinamul	5	5	5	5	5	5	5	5	5	5
Plexigum M80	1	5	2	2	5	1	5	2	3	5
Plexigum 380	1	5	1	1	5	1	5	2	4	5
Plexigum 74	5	5	5	5	5	5	5	5	5	5
Plexigum 75	1	5	2	1	5	1	5	2	2	5
Plexigum 5484	1	5	2	1	5	1	5	2	1	5
Pioloform BL	1	3	4	1	3	1	4	2	1	5
Pioloform BM	2	3	4	1	3	1	4	2	2	5
Témoin	4	5	1	5	5	4	5	4	5	5

Produit	Argent				Plomb			
	CT	UV	CO2	SO2	CT	UV	CO2	SO2
Synocryll	1	4	1	5	1	4	1	3
Paraloïd B48N	1	3	1	4	2	2	2	4
Paraloïd B72	1	4	1	2	1	3	1	4
Incralac	1	4	1	4	2	2	2	2
Pentarol 100	4	4	4	5	3	2	4	5
Rhodopas M	1	4	1	4	1	3	1	5
Sicomet brillant	1	4	1	4	2	2	2	2
Sicomet mat	1	5	1	5	2	2	4	5
Paraffine	1	1	4	3	3	3	2	5
Cire Miné. Blanc	1	1	4	3	2	2	2	4
Cire jaune	4	5	5	4	3	4	3	3
Cire Microcrist.	1	5	4	3	3	3	4	4
CE 1170	1	4	1	2	1	4	1	3

Résultats

Le Fer:

Parmi les produits testés pour le fer on remarquera que :

- a. Un seul produit résiste partiellement au brouillard salin et au gaz sulfureux: le Paraloid B48N. Deux autres produits résistent au brouillard salin: les Piloform BL et BM.
- b. Après essais en chambre humide précédé d'une exposition aux UV nous constatons que seules les cires blanches et microcristallines ainsi que la paraffine résistent aux UV (absence de corrosion par l'humidité sur les éprouvettes, signe d'une non destruction de la couche protectrice par les UV).
- c. Pour les essais en multicouche nous constatons après 144 heures de brouillard salin que les éprouvettes enduites de Paraloid B48N et de cire minérale blanche ainsi que celles enduites de Sicomet brillant et de cire minérale sont presque exemptes de corrosion.

Le Cuivre:

- a. Un seul produit résiste au brouillard salin le Rhodopas M mais que ce même produit est sensible aux UV, au SO_2 , au CO_2 et aux chocs thermiques!
- b. Le CE 1170 est également intéressant puisqu'il semble résister à tous les tests sauf à celui du brouillard salin.
- c. Un dépôt de rhodopas suivit d'un dépôt de cire minérale blanche ou de paraffine résiste parfaitement à 144 heures de brouillard salin (0% de corrosion), il en est de même avec l'Incralac revêtu de cire minérale blanche ou de paraffine. Dans les deux cas cependant l'aspect avec la cire minérale est plus agréable à l'oeil.

L'Argent:

- a. Parmi les quelques vernis testés, le Paraloid B72 semble donner les meilleurs résultats au brouillard salin. Il est malheureusement détruit par les UV dans les conditions décrites plus haut.
- b. En atmosphère chargée en soufre, c'est, en revanche, la cire minérale blanche et la paraffine qui donnent les meilleurs résultats, quand on sait que ces produits résistent également aux UV on peut se demander s'ils ne sont finalement pas mieux adaptés.

Le Plomb:

- a. L'Incralac, et le Sicomet brillant, s'il ne sont pas les plus performants, sont les plus réguliers dans leurs résultats. Là encore beaucoup d'essais restent à effectuer, notamment ceux au brouillard salin.
- b. Le CE 1170 lui aussi donne d'assez bons résultats d'ensemble bien que l'on puisse déceler une certaine fluorescence du produit.
- c. Le témoin, quand il n'est pas exposé au SO_2 réagit aussi bien et souvent mieux que les échantillons vernis.

En conclusion nous pouvons tirer les enseignements suivants:

1. Le même produit de protection ne peut pas être utilisé sur tous les supports.
2. Le même produit de protection est rarement adapté à tous les types d'environnement, il faudra donc sélectionner la protection en fonction de cet environnement.
3. Le même produit de protection exposé aux mêmes sources de vieillissement sur un support identique est moins efficace quand il est déposé sous vide que quand il est déposé à la pression atmosphérique normale, sauf pour les chocs thermiques.
4. La totalité des vernis (cires et paraffine exclus) sont détruits par les rayons ultraviolets dans les conditions de l'expérience.
5. Pour le plomb, en absence de SO_2 , la non protection des surfaces semble aussi, et parfois plus, efficace que la protection à l'aide d'un vernis ou d'une cire.

6. La meilleure protection semble être celle obtenue par l'utilisation d'une bi couche puisque l'aspect du cuivre est inchangé après 144 heures en brouillard salin et les ferreux sont également mieux protégés. Des essais restent à effectuer avec les acétates de butyrale qui semblent donner d'excellents résultats même sans double couche protectrice (tableau n°3).

Tableau n° 3. Essais réalisés en multi-couches. Aspect après 144 heures de brouillard salin (mêmes échelles que pour le tableau n° II). N.B. C.M.B. = Cire minérale blanche.

Produit	Fer	Cuivre
Paraloïd B48N + C.M.B.		4
Paraloïd B48N + Paraffine	5	3
Paraloïd B72 + C.M.B.		4
Paraloïd B72 + Paraffine		5
Incralac + Paraffine	5	1
Incralac + C.M.B.	3	1
Rhodopas M + Paraffine	5	1
Rhodopas M + C.M.B.	2	1
Sicomet brillant + Paraffine	1	3
Sicomet brillant + C.M.B.	2	2
Synocryll + Paraffine	4	2
Synocryll + C.M.B.	3	2

Le problème qui peut alors se poser est un problème d'épaisseur du revêtement total, donc un problème d'esthétique. Cependant les épaisseurs mesurées restent "raisonnables" puisqu'elles se situent entre 15 et 45 microns pour le cuivre et 80 à 93 microns pour les fer. De plus, la cire a un effet "matifiant" plus agréable à l'oeil.

Perspectives

Les essais commencés il y a bientôt huit ans sont loin d'être terminés et beaucoup de produits restent à tester. Les études sur les possibilités présentées par l'utilisation de couches successives de vernis ou de vernis et de cires (de cériques en général) sont très prometteuses notamment en milieu salin.

Nous souhaitons également, à la lueur des résultats obtenus, tenter de faire des mélanges de vernis, quand ils sont possibles, pour optimiser la protection, le but final étant, naturellement, l'application sur les objets archéologiques. Comme cela nous a été suggéré, d'autres sources de vieillissement peuvent également être utilisées comme, par exemple l'hydrogène sulfureux ou l'aldéhyde formique, de même les conditions de dépôt des revêtements peuvent faire l'objet de multiples modifications ainsi que l'enchaînement des essais et le nombre d'alliages de métaux.

Le problème majeur de cette étude réside dans le fait que pour chaque essai, cinq échantillons de chacun des produits testés sont nécessaires, la multiplication des paramètres entraînera une multiplication des échantillons. Par exemple l'addition de quatre paramètres nécessite la préparation de 9.200 échantillons supplémentaires pour les quatre métaux étudiés soit environ 2.300 heures de travail.

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8. Torraca, G., *Solubility and solvents for conservation problems*, ICCROM, Rome, 1990.

Notes

a. Fournisseurs des matériels:

- Dermatron D8, Sté Engelhard Industries France, 4 rue Beaubourg, 75004 Paris, France
- Enceintes de vieillissement:
 - + Chocs thermiques, Brouillard salin et étuve UV: Le Matériel Physico-Chimique FLAM et Cie, BP 45 Z.I des Chanoux, 93300 Neuilly-sur-Marne, France
 - + Gaz sulfureux et gaz carbonique: Bioblock Scientific BP 111 Illkirch CEDEX, France

b. Fournisseurs des revêtements:

- + Rhodopas M, Paraffine, Cire minérale blanche, Cire jaune et cire microcristalline: Prolabo, 12 rue Pelée, 75011 Paris, France
- + Synocryll: Sté Cray-Valley, 25 rue St Hilaire, 95310 St-Ouen-l'Aumône, France
- + Paraloïd B 72 et B 48N: Röhm and Haas, 185 rue de Bercy, 75579 Paris, CEDEX 12, France
- + Incralac: Incralac Inc. 825 Third avenue, New York, N.Y. 10020, USA
- + Pentarol 100: Franck Joel Ltd, 5, Oldmedow Road, Hardwick Industrial Estate, King's Lynn, Norfolk PE30 4HL Grande Bretagne
- + Blackor: Blackson, 42 bis rue du vieux pont de Sèvres, 92100 Boulogne, France
- + Sicomet: Sté Sicof
- + Tetenal: Tetenal Photowerk, Postfach 2029, 2000 Norderstedt, Allemagne
- + Noverox: Ets R. Brendlé et C° 103 rue de Strasbourg, BP 309 68305 St. Louis CEDEX, France
- + CE 1170: CONAP, 1405 Buffalo Street, Olean, New York 14760, USA
- + Vinamul: Vinamul SA, 92504 Rueil-Malmaison CEDEX, France
- + Plexigum: Röhm GMBH Chemische Fabrik, Postfach 4242, 6100 Darmstadt 1, Allemagne
- + Pioloform: Wacker % CODIM, 40 rue Lauriston, 75116 Paris, France

Abstract

This paper describes a test set up between three institutions to consider different conservators' assessments of the condition of archaeological iron. The results indicate that there is no guarantee of consistency between institutions or individuals in judging condition.

Keywords

Condition, survey, archaeological, iron, conservation, assessment, statistics

Assessing the Condition of Archaeological Iron: An Intercomparison

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Introduction

Assessing the condition of objects is central to the conservators' role. It is the first step to deciding what is wrong with the object and how to treat it. Carrying out surveys of the condition or the conservation needs of a whole or part of a collection is a function of conservators in most museums. Such surveys provide data for application for improvement grants or to assess conservation needs and plan work loads.

Recently in the UK the use of the condition survey as a management tool has been promulgated (1,2). In this guise the condition survey is used to determine how effectively a museum is caring for its collection. It is used to show whether the quality of care has improved, as seen by an overall movement towards improved condition, or decreased, as seen by an overall movement towards worse condition.

In the British Museum, conservation surveys of discrete parts of the collection have been carried out for many years. The objects are assessed for conservation priority and an estimate of the amount of time required for the conservation work made. Such surveys do not necessarily require to be carried out frequently, but can take a large amount of time. They provide a lot of useful data for both museum managers and conservators.

Condition surveys differ from conservation surveys in that the only assessment made is of the condition. In her model Keene (2) utilises a statistical approach where the condition and damage type of a subset of the objects are assessed. From this data a calculation of the gross conservation time needed for the whole collection can be made. The conservation implications for each object are not assessed. Such surveys can be carried out in a defined period of time because of the need to record only a minimal amount of data, and can therefore be carried out on a frequent basis, for instance once a year, to see how the condition of a collection is changing.

If surveys are to be repeated and their results compared, the basis on which the work is carried out must be consistent. The problem of achieving consistency is not tackled by either the Office of Art and Libraries (OAL) (1) report or Keene (2), but the latter recognises this problem when she states that the 'magnitude of differences in perception are not known'.

Two different experiences led the authors of this paper to the conclusion that consistency among conservators cannot be guaranteed. The British Museum's collection of cuneiform tablets was surveyed in 1987 and 1990 (3,4). In the first a large proportion of the tablets was specified as having a high conservation priority. In the second survey the proportion of objects in the high conservation priority group was greatly reduced. The number of tablets conserved in the intervening years did not account for the difference in the proportions. This appears to be attributable to the background of the conservators concerned and the adoption of different standards in judging the condition of the tablets.

In the last two years two of the authors, Newey and Bradley, have been investigating the possible use of 'the plasma' treatment for archaeological iron in the

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Museum. As a part of the investigation they looked at many archaeological iron objects in the collection, and formed a view about the condition of objects. They assessed objects with a particular physical appearance as being in a stable (good) condition and in no immediate need of conservation. On a visit to the Museum of London, Bradley was shown iron objects with the same physical appearance which were judged unstable and in need of conservation by the Museum of London conservators.

The implications of this lack of consistency in judging condition on the conduct of surveys, whether condition or conservation, was considered worthy of investigation. This was particularly timely as the authors were embarking on a survey of the Museum's holdings of archaeological iron, and it was likely that several conservators would be involved in the work. The implications of conservators from different institutions arriving at different judgements of condition was also of concern since this could affect the conclusions of research into deterioration, the effectiveness of stabilisation methods and storage methods.

In order to determine whether different conservators made different judgements and whether there was an institutional bias, a blind test was set up. The purpose of the test was for conservators from three institutions, the British Museum (BM), The Museum of London (MOL) and the English Heritage Ancient Monuments Laboratory (AML) to judge the condition of a group of objects with which they were mostly unfamiliar. In the test, four categories of condition were used as the basis for the assessments since four categories were in use in many institutions in the UK. A control group of British Museum staff, only one of whom had conservation experience, participated.

Object condition categories

Conservators from a number of institutions have independently come to the conclusion that four categories of condition or conservation priority are most suitable for the purposes of the surveys. This is probably because it is fairly easy to identify stable objects in need of no treatment, and those that are unstable, either physically or chemically, and require immediate conservation. The condition of the remaining objects is more difficult to judge, but the problem is overcome by defining two further categories based essentially on physical and chemical stability.

During surveys of the collections in the BM, the condition and conservation requirements of the objects were recorded to provide information for immediate and future use. Lengthy descriptions of each object were time consuming and, in many cases unnecessary, and so a system of four condition/conservation categories was devised, as follows.

- A. No work needed.
- B. Low conservation priority (in stable condition, but some work desirable when other priorities and/or resources permit).
- C. Medium conservation priority (not in immediate danger, but needs essential work).
- D. High conservation priority (eg active deterioration).

Other institutions in the UK have promulgated categories of condition. The Horniman Museum, London (5) describes four categories as:

- Good: Objects that are in a stable state not requiring any attention at that time.
- Fair: Objects with slight problems that will need attention in the future.
- Urgent: Objects that need attention as soon as possible.
- Immediate: Objects that need attention immediately.

At the MOL the archaeological conservators use four working definitions.

- 1. Will deteriorate unless treated.
- 2. Deteriorating and needs substantial work before archiving.
- 3. Not deteriorating, archivable but needs some work before display/publication.
- 4. Little or no work needed before display/publication.

This differs from other definition lists, in that the first category is the worst condition.

Keene, in her research project on collection condition surveys for OAL, also describes four categories C1–C4. Here each object is seen in the context of its collection and judged on that basis.

- C1. Good, in good conservation condition and is stable.
- C2. Fair, disfigured and damaged but stable—needs no immediate action.
- C3. Poor, poor condition and/or restricted use, and/or probably unstable, action desirable.
- C4. Unacceptable, completely unacceptable condition.

It is also worth mentioning at this point the ordering of the categories. At the BM a copy of the survey report is sent to the relevant Department of Antiquities for their information. The original order gave A as the number or percentage of objects requiring immediate treatment and hence in the worst condition, B the next most urgent, C those to be treated when resources permit and D requiring no work at all. It was found that the recipients of the reports had often read no further than Category A and it appeared to them, often wrongly, that the collection was in a poor state because the order focused on the negative aspects of the results. It was decided to reverse the order so that A now describes the objects requiring no work at all and D describes the group most in need of conservation. Other conservators had also found this, and it is becoming standard practice to list the results in order of good to bad.

Setting up the comparison

The individuals participating in the test were: from the BM, eight metal conservators and the control group of five consisting of a conservator turned administrator, two conservation scientists, a statistician and an intern; from the MOL, seven archaeological conservators; and from the AML, two archaeological conservators.

When planning the assessment session it was decided to use a sample of between forty and fifty objects covering a wide range of object conditions. Fifty objects was felt to be the maximum number the test would be able to deal with. Nineteen objects were selected from the BM and thirty-one from the MOL by one member of staff in each institution. The aim was to ensure that the range of objects was similar in age and provenance between the two institutions' selections. Although some of the participants might have seen some of objects at some time before the session it was possible to evaluate the effect of possible bias in the analysis of the results.

The MOL collections reflect the archaeology and history of London and have all been found within the boundaries of the City of London. Consequently objects from the BM were selected from the collections of the Departments of Prehistoric and Romano-British Antiquities and Medieval and Later Antiquities rather than the Classical and Oriental Departments. It was also hoped that the objects might mirror the range of acquisition sources of the collections, such as recently excavated, historic collections given or purchased in the nineteenth and twentieth centuries, provenanced and non-provenanced objects. Several different types of objects, many previously conserved, were chosen, including metal and non-metal composites.

One of the aspects to be considered was the extent to which knowledge and experience gained from a given institution's collections could be extrapolated to another collection. This is of immense importance when considering the validity of condition surveys carried out on a collection by outside conservators.

Organisation of the test

On the day of the intercomparison, a large table was covered by sheets of paper numbered 1–50 in a spiral arrangement, and small pieces of paper, also numbered 1–50, were placed in a bucket and shaken up. As each object was taken out of its container it was assigned a number taken at random from the bucket, and

was placed on the corresponding sheet. The details of the object were noted, after which it was covered up until the start of the intercomparison.

The aim of this arrangement was to avoid grouping together objects of a similar type or from the same source so that 'memory effects' due to the surveyors recognising their own objects would be minimised. As it turned out the degree of mixing appeared not to be complete, as some runs of consecutive numbers were drawn. However, this presented little problem as the spiral arrangement of the sheets ensured a sufficient overall degree of randomness.

The definitions of conservation/condition used by the BM and reported by Keene were posted on a wall. After introductory remarks about the aims of the intercomparison, the surveyors were asked to assess each object in any convenient order into categories A–D following the British Museum convention, and to write their results on a proforma along with a score (1–3) representing the degree of difficulty in assessing each object, and any comments they wished to make. (The degree of difficulty scores turned out to be difficult to interpret and so they have been ignored in what follows.) The participants were asked to complete their survey without consulting each other, and within a time-limit of fifty minutes. This time-limit was decided on assuming that one minute would be needed to assess an object, and was about right, as it allowed everyone to finish without rushing. A general discussion followed on the problems encountered during the survey.

Results

The raw data (6) indicated that any particular object can be assessed in very different ways by different people. It also gave the impression that staff of a given institution tend to have relatively similar views. The aim of the statistical analysis was to investigate these observations in more detail.

The first step was to compute a disagreement index by assigning a score of 1 for an 'A' assessment and 4 for a 'D' assessment, and computing the Euclidean distance (sum of squares of differences) between each individual on the basis of these scores. A technique known as non-metric multidimensional scaling was then used to approximate the dissimilarities in the form of a plot (Figure 1). In this type of plot, dissimilar individuals are far apart, and similar individuals are close to one another, though it should be borne in mind that the plotted distances are not proportional to the Euclidean distances but preserve only their rank orders (hence the term 'non-metric'). This technique is well-known in market research for comparing consumers' views of commodities, a similar application to the present one. Further details can be found in Krzanowski (7).

Although all dimension-reducing plots involve a degree of distortion (measured by a statistical quantity known technically as 'stress'), the main feature is very clear. There is a marked difference between the two main groups of conservators with the 'control' group generally similar to the BM conservators.

To put this in more practical terms, the percentage that each individual considered was in need of conservation (ie fell into categories B–D) was computed and is shown in Figure 2. This indicates that the MOL conservators regarded the objects as generally more in need of conservation than the BM conservators (with the BM control group having fairly similar views to the BM conservators). The AML conservators were both relatively optimistic about the condition of the objects, but as there were only two they cannot necessarily be regarded as typical. The mean and standard deviation of results in each institution are given and, on the basis of these, Figure 1 can be interpreted as showing a continuum from optimism to pessimism about the state of the collection; relatively deviant views occur offset to either side of this trend. The typical standard deviation in the percentage assessed as B–D, within an institution, is 9%.

Discussion

As there were unequal numbers of MOL objects and BM objects, a bias could have been introduced if staff had recognised their own objects and viewed them differently in some way. To test this, a two-factor analysis of variance was

performed on the results for the BM and MOL conservators, dividing the objects into groups according to their source. The individual person was not considered as a factor, it being assumed that assessments were representative of the institution, and that they were formed independently for each object. Table I shows the percentage of objects classed as B-D for each of these subgroups, with the number of individual assessments in each subgroup in brackets.

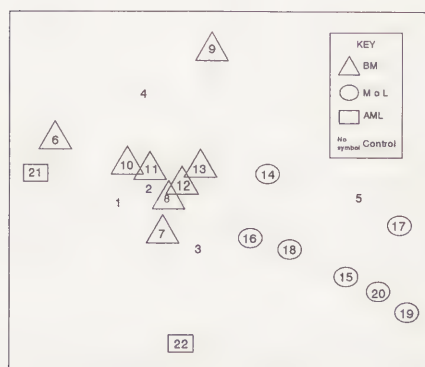
Table I. Percentage of objects assessed as B-D.

Source of object	Conservators		All BM/MOL conservators
	BM	MOL	
BM	72% (8)	90% (7)	81% (15)
MOL	64% (8)	81% (7)	72% (15)
All objects	68% (16)	85% (14)	76% (30)

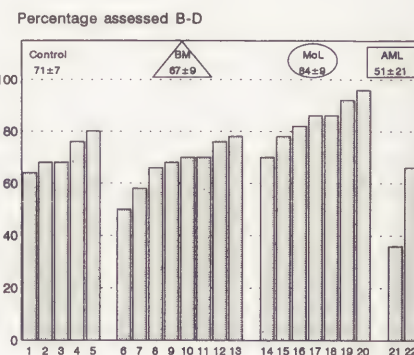
The thirty individual percentages were tested in an analysis of variance, after arcsine-square root transformation. This is necessary for ensuring approximate normality of the values (8). The analysis showed that there was a statistically significant difference (at approximately the 5% level) in the condition, on average, of the BM and MOL objects selected for this survey, the BM selection being considered to be in a relatively worse condition. The analysis also confirmed (at approximately the 1% level) the already noted difference in the view of the conservators from the two Museums, the MOL staff taking a more pessimistic view of the collection as a whole.

These differences are fairly evident from the raw percentages in Table I, and a more interesting point is that there was no statistical 'interaction' between the source of the object and the institution of the conservator. We can thus conclude that any differences between the institutions are not influenced in any major way by the particular balance of objects represented or by any subconscious prejudice by surveyors against or towards their home institution's objects.

A further feature which is relevant to the interpretation of the individual similarities shown in Figure 1, and to possible reasons for the observed effects, is the fact that certain pairs of individuals have very similar views. Among the BM staff, 8 and 2 shared very similar opinions, as did 10 and 11; among MOL staff, 19 and 20 were also in relative agreement. This agreement is not only on the percentage requiring treatment but also on the condition of each individual object. Observations of this type, based on an agreement index, could be relevant to the choice of staff to perform surveys, depending on how far consistency is a priority.



1. Non-metric scaling configuration for assessment data. The numbers 1-22 refer to individual assessors, the symbols to their institutions. The closer two individuals are on the plot, the more closely they tend to agree on the condition of individual objects. Stress 20%.



2. Barchart showing the percentage of the 50 objects each individual assessed to be in need of conservation. Individuals are numbered as in Figure 1. The mean and standard deviation for each institution are given.

Conclusions

This study has shown that there are significant differences between two institutions for which there were sufficient participants to judge (MOL and BM) in the way that they assess the condition of objects in a collection and hence judge their conservation needs. The discussion held after the intercomparison suggested that this was at least partly due to the slightly different wording of the assessment criteria in use at the two institutions. Within institutions it is possible to identify small groups of individuals who are internally consistent, and also individuals who differ from the majority opinion.

The results are also relevant to the conduct of sampling schemes. In addition to observing significant differences between institutions this study has also shown that interpersonal variation within institutions cannot be ignored. This needs to be taken into account in sampling calculations, even when surveys are arranged 'in-house'.

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Abstract

High quality silver artifacts which had belonged to ancient nomads (Sarmatians) that became embrittled as a result of burial conditions were studied. The processes taking place during annealing in the course of conservation of the artifacts were also studied. Metallography was the main research method of the study. Intercrystalline corrosion was shown to have resulted in brittleness. During annealing, partial recovery of ductility occurred due to coagulation of corrosion products and recrystallization. Annealing conditions were recommended.

Keywords

Brittle silver, metallography, intercrystalline corrosion, annealing, recrystallization, coagulation

Annealing of Brittle Archaeological Silver: Microstructural and Technological Study

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It is well known that archaeological silver can be extremely brittle, even if the surface bears no traces of destruction. Consequently, brittleness is associated with variations in the inner structure of silver. Werner relates these variations to the phenomena in three ways: relaxation of grain boundaries because of intercrystalline corrosion, natural ageing—lead precipitation from a supersaturated silver-lead solution, and coarse grain size (1). In the opinion of Thompson and Chatterjee, the main reason for brittleness is natural ageing, involving precipitation of lead remaining after supersaturated solution quenching. The lead then precipitates in a finely-dispersed form later under burial conditions; this causes embrittlement (2). It is common knowledge that lead is the chief impurity of ancient silver, produced by cupellation from lead-silver ore. Schweizer and Meyers showed that brittleness could result from precipitation of copper from the supersaturated silver-copper solution; this is related to natural ageing during long exposures to soil of buried artifacts (3).

In order to restore the ductility lost by brittle archaeological silver, researchers recommend annealing it at temperatures that bring about dissolution of the brittle phases (copper and lead) and enables their transition to solid solution (2, 3). Conservation practice shows that silver annealing can partially restore ductility. According to Plenderleith's recommendations, brittle silver can be heated to 250–400°C to give it strength, and heated to 600–650°C to restore ductility. Organ restored the ductility of brittle silver by annealing at near melting point temperatures in a layer of charcoal; Werner did the same by heating the metal in hydrogen to 300–400°C (4, 1). Thus, at the present time, extensive data on the investigation of brittle archaeological silver have been accumulated, but some problems are still not clearly understood. Specifically, modifications in microstructure of brittle alloys may occur after annealing at different temperatures. It is not clear how the metal structure of the artifact changes after annealing. If these changes are essential information stored in alloy structure, this information can be partially or entirely lost.

We faced the problem of brittle silver when treating two paired Sarmatian plaques (2nd century B.C.) which were found in the Volga basin by the expedition of I.A. Fedorov-Davydov. The plaques were badly distorted, were broken into fragments, and had lost their ductility. The artifact thickness was 0.5–1.0 mm. Unbending and strengthening of the fragments required annealing. The great number of fragments available made it possible to study the cause of brittleness and the effect of annealing on the reclamation of ductility. Metallography, employed successfully in other studies, served as the main research method in the present work (1–3). In order to carry out a metallographic examination, the specimens were embedded in plastic (setting at room temperature) and were polished with different emery papers. They were then polished with a fine suspension of chrome oxide in water. The etching solution was 20 g of chrome oxide, 1.5 g of sodium sulphate in 100 ml of water. We have described the peculiarities of etching brittle archaeological silver in detail elsewhere.

The microstructure of the initial brittle fragments consisted of small (20–50 microns), recrystallized grains with a large number of annealing twins (See fig. 1). The grain boundaries were thickened with cracks that propagated along some of the boundaries. It could be concluded from the appearance of the microstructure that brittleness was due to relaxation of grain boundaries. The nature of the microstructure also suggested that the artifact had been made of high quality silver containing not more than 8.8% of copper (the limit of copper solubility in solid solution at eutectic temperatures) by means of hammering and annealing.

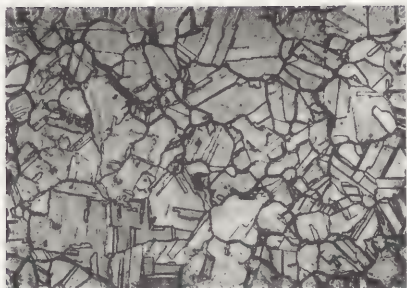


Figure 1. Microstructure of plaque in the initial brittle state (magnification 300×).

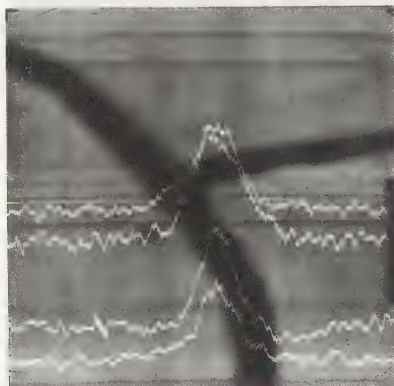


Figure 2. Profiles of characteristic X-ray radiation intensities, showing K-lines for copper, chlorine, zinc, and calcium. (magnification 10,000 \times).

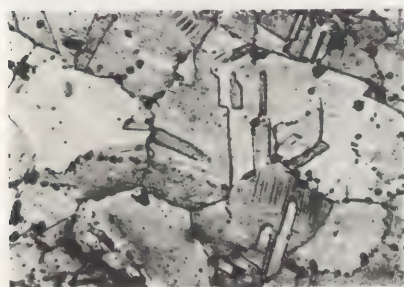


Figure 3. Microstructure of the plaque after a 700°C, 30 minute annealing under a charcoal layer (magnification 300 \times).

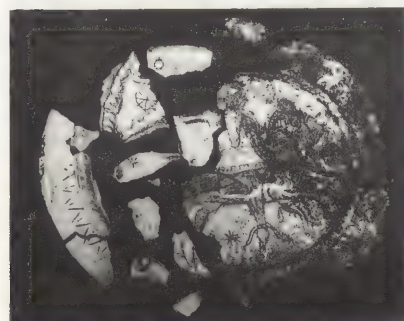


Figure 4. (a) Plaque during conservation, and (b) after conservation.

Traces of dendritic segregation were not observed, that is, it could be supposed that the initial stock had been not an ingot but a plate. Judging from fine grain size, the final annealing was performed at relatively low temperature (not more than 700°C).

The composition of the artifact was determined using atomic spectroscopy (Perkin-Elmers device); main impurities were copper (0.49%), zinc (0.015%), gold (0.6:3%), and magnesium (0.02%); it was not possible to determine the lead content. For a more detailed microstructural study, the fragments were examined using a scanning electron microscopic (3SM-BM scanning electron microscope). The brittle silver grain boundaries were enriched with copper, zinc, chlorine, and calcium (the latter was not determined when analysing the chemical composition of the alloy) (See fig. 2). The relaxation of grain boundaries was attributed to intercrystalline corrosion, which caused the formation of chlorides along grain boundaries.

The annealing of the fragments in air at 700°C for 30 minutes in an electric muffle furnace, as well as under a layer of charcoal, resulted in a considerable rise of ductility in both cases. It was accompanied by the changes in the microstructure depicted below. After annealing in charcoal phase, globules appeared on the grain boundaries and a certain grain coarsening occurred. As this took place, the old grain boundaries became intensified at the expense of coagulated phase but remained at their location (See fig. 3). Air annealing was accompanied by the same effect on grain boundaries, but with simultaneous complete inner oxidation in the specimens and formation of oxide particles visible under the microscope.

Examination with the electron microscopic of the fragment annealed under the charcoal layer showed that globules on the grain boundaries consisted of the same elements as the products of intercrystalline corrosion on prior grain boundaries of brittle silver. Thus, coagulation of corrosion products occurred during heating. It is apparent that this phenomenon, accompanied by grain size growth and grain boundary movement, that is, recrystallization, is responsible for the increase in ductility. The plaque was successfully restored and strengthened by means of annealing in charcoal at 700°C for 30 minutes by the restorer M.S. Grinkrug) (See fig. 4).

In order to determine the extent to which the regularities of modifications in structure are common in nature, we studied fragments of other artifacts of the Sarmatian times which were received for conservation. Three of these objects were a vase found in the Sokol grave (3rd or 2nd century B.C.), a vessel from the Krasnodar region (4th century B.C.), and fragments of the pole top from the same region (4th century B.C.). All of the artifacts had been hammered from high quality, thin plate silver. The silver was badly embrittled, and its microstructure displayed recrystallized grains of various sizes in the different artifacts and cracks propagating along the grains. The microstructural modifications during annealing at 700°C were accompanied by the same transformation on the grain boundaries as in the plaque.

For more detailed study of the effect of temperature, time, and atmosphere of annealing on changes in microstructure and properties of brittle silver, the fragments of the pole top were annealed starting from 300°C, to near the melting point (50°C below the melting point of the alloy) under a layer of charcoal in an electric muffle furnace in air. The annealing cycle was 15 minutes, and the temperature was varied at 50° degree intervals.

The annealing at 500–600°C under the charcoal layer brought about no changes in the microstructure or properties of the material. Coagulation of corrosion products occurred at 600°C on the grain boundaries, as well as increased silver ductility. Similar changes in microstructure were observed with annealing at 650–850°C, but the globule size on the grain boundaries somewhat increased at 800–850°C. However, a considerable rise of ductility did not take place. Only at 900° (the melting point for the alloy is 930°C) did the ductility grow to a substantially. The microstructure exhibited the following changes: a new system of grain boundaries emerged, the number of globules was drastically reduced,

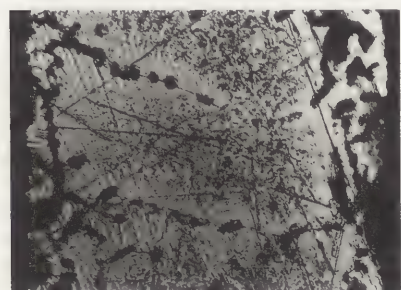
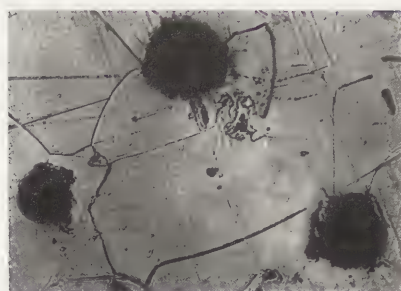


Figure 5. (a) Microstructure of the pole top specimen after a 700°C, 30 minute annealing, under the charcoal layer, and (b) in the air (magnification 300×).

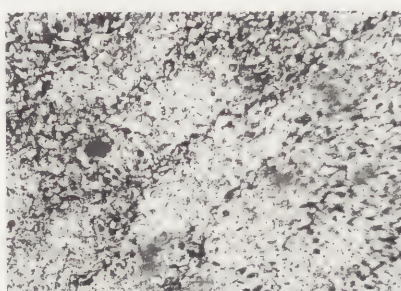
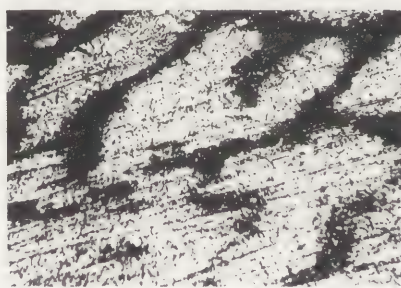


Figure 6. (a) Microstructure of the buckle fragment (Krasnodar region, 16th century) in the initial brittle state, and (b) after a 700°C, 15 minute annealing under a charcoal layer (magnification 300×).

and their size increased significantly (See fig. 5a). Many globules were accumulated not on the grain boundaries but within grains with recrystallized regions often appearing near the globules.

The annealing of the same specimens in air showed the findings given below. The formation of inner oxidation zones was observed along the grain boundaries and in the subsurface zone of the fragments. These zones retarded the coagulation of corrosion products, since the oxides formed during oxidation were so dispersed that they could not be observed using conventional magnifications, and only an interface between oxidized and non-oxidized zones was noted. The alloy properties did not vary. Coarsening of oxide particles that was accompanied by phase coagulation on grain boundaries occurred at 700–900°C, but cardinal restructuring (as it was observed at 900°C while annealing under the charcoal layer) did not take place (See fig. 5b). A considerable increase in ductility did not occur either. In order to study the kinetics of ductility recovery, the fragments were heated in a mixture of sodium chloride (33%) and sodium sulphate (67%) for 5, 10, 20, and 40 minutes at 650°C. Ductility recovered within just five minutes of the start of the heating, and did not increase with time of holding.

A comparison of annealed properties for similar size fragments treated in salt and in an electric furnace under a charcoal layer for 20 min showed that the rise of ductility was equal for them; that is, the heating rate had no effect on the improvement of the properties of the samples. Judging from these experiments, it can be concluded that in order to increase ductility, short-time heating of brittle archaeological silver of high quality under a charcoal layer at 600–700°C is sufficient. If the rise in ductility is inadequate, the temperature can be increased to a higher level (up to 50°C below melting point of alloy). In doing so, heating in an atmosphere that offers protection against oxidation is essential. The results obtained coincide with the recommendations given in the studies of Werner, Plenderleith, and Organ (1, 4).

However, is it appropriate to apply annealing to all artifacts made of brittle silver, or should it be used only in cases when unbending or strengthening of an artifact is required, as no guarantee of its strength can be given without annealing? This question was posed due to those changes in microstructure which were observed during the study of different specimens from brittle archaeological silver.

Thus, during a 700°C, 15 minute annealing of an artifact that contained traces of dendritic structure (along which corrosion took place) on a background of fine polyhedrons (See fig. 6a), we observed the disappearance of these traces as well as the concentration of corrosion products into nets (See fig. 6b). Information on the technology of manufacturing an artifact which was stored in its primary structure was then lost.

During a 700°C, 15 minute annealing of a specimen with traces of discontinuous precipitation along the grain boundaries where preferential corrosion occurred (See fig. 7a), we observed formation of globules at the point of precipitation (See fig. 7b). Again, evidence indicative of the conditions of prior processing of an artifact is also eliminated in this case. Therefore, we think that in order to give strength to artifacts made of brittle silver, annealing must be applied only in cases of vital necessity.

Conclusions

Specimens of high quality silver artifacts of the Sarmatian times (4th–2nd centuries B.C.) were studied. It was determined that they had been produced by hammering of plate stock and had the polyhedronic structure of annealed metal.

It was determined that intercrystalline corrosion resulted in brittleness. The corrosion was accompanied by concentrations of chlorine and calcium, together with copper and silver impurities on the grain boundaries.

Redistribution of corrosion products occurs during annealing at temperatures of 600°C and above, accompanied by the formation of globules on the grain boundaries. Also, the system of grain boundaries becomes restructured; this is occa-

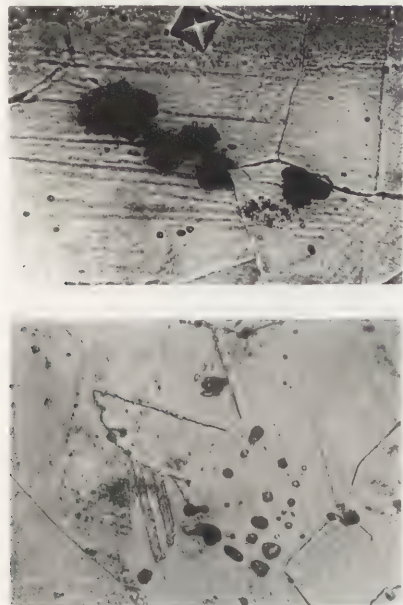


Figure 7. (a) Microstructure of the pole top fragment with traces of discontinuous precipitation in the initial brittle state, and (b) after a 700°C, 15 minute annealing under a charcoal layer.

sionally accompanied by grain growth, and leads to an increase in ductility of an artifact.

To prevent the inner oxidation of the alloy, annealing should be performed in an atmosphere that protects against oxidation. The recommended annealing cycle is 5–10 minutes.

Annealing results in changing the microstructure; that is, grain growth and disappearance of traces of dendritic segregation, or signs of discontinuous precipitation which were affected by preferential corrosion. Because of this, information stored in the prior structure of an artifact is lost. It is apparent that annealing should be applied only in cases of urgent necessity.

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Abstract

A new model that takes account of both tin and copper in the alloy is proposed to improve the understanding of deterioration processes of outdoor bronze sculptures. The corrosion mechanism relates to the selective dissolution of copper. Two main processes occur: the process of tin oxidation with the formation of insoluble tin compounds which remain in the corrosion film, and the process of copper oxidation with the migration of copper ions to the surface. Considering this mechanism, mechanical action, and the acidity of the precipitations, two different evolutions at the surfaces are suggested. On the surfaces directly exposed to the rain, copper ions are washed out leaving a tin-rich external layer. A cyclic corrosion process is engaged. In the unexposed surfaces, the outermost layer is formed with well-known copper corrosion products. This model can be used to establish the degradation state of outdoor bronze sculptures for a new conservation approach.

Keywords

Atmospheric corrosion, bronze, conservation, corrosion products, outdoor sculpture

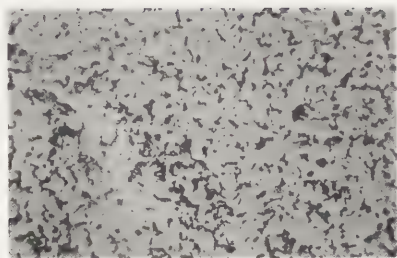


Figure 1. Macroscopic view of black spots surrounded by green pale corrosion products, porous and unprotected.

New Model of Outdoor Bronze Corrosion and Its Implications for Conservation

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Introduction

The purpose of this present paper is to outline a general framework for the understanding of the corroded surfaces of outdoor bronzes. Due to the increase in the pollution level of the atmosphere, the patinas on outdoor bronzes are now generally unstable. This can be observed by green trails on the stone basements due to the dissolution of copper. Numerous papers explain the bronze corrosion process by applying the copper corrosion model which leads to the following corrosion structure: a green outermost layer of copper II compounds (generally hydroxysulfates) and an internal layer of copper oxide located on the unattacked alloy (1-3).

The model described here was established from several investigations of outdoor bronze sculptures such as Rodin's bronzes, a Stanislas statue in Nancy, France, and other bronzes exposed to urban atmospheres (4-6). In these studies, different analyses were performed to correlate the nature of the corrosion products and their location with exposure conditions. The nature of patinas and their chemical characteristics will be reviewed first. Then, this information will be used to propose a qualitative mechanism for the growth of corrosion layers.

Some aspects of the problem cannot be presently specified with rigor. The semi-quantitative assessment of the formation of corroded surfaces represents a step towards a more complete understanding of the corrosion processes. This paper will make frequent reference to published works on copper patina formation (7).

The nature of corrosion products

Analysis of corrosion products on outdoor bronzes (Cu-Sn alloys) revealed numerous copper compounds which have their own characteristics, depending on surface orientation and the conditions of atmospheric exposure. Characterization of the corrosion products' thermodynamic stabilities and research on their formation kinetics have already been published (8-11). Little is known about the corrosion products of tin. They are generally not identified in the bronze patinas. Nonetheless, recent results [4,5,6] show that the corroded surfaces may be classified in relation with their aspect (colour, morphology, hardness) and composition. The different surface categories are related to the rainfall exposure conditions. The results are summarised in Table I.

Two types of surfaces may be distinguished: those exposed to rainfall, and those protected from this effect. The first category in the table lists results for surfaces exposed to rainfall. They are made of pale green products and black areas which stand as islands surrounded by the pale green products (figure 1). As already mentioned by Weil *et al.*, the pale green areas act as anodes and the black areas act as cathodes (12). Elementary analysis reveals that the surface compounds have a high tin element content. X-ray diffraction or infrared spectrometry analysis show that the copper compounds are mainly brochantite and seldom antlerite.

The second category in the table outlines results for the surfaces that are not

Table I. Comparison between main types of corroded surfaces of the outdoor bronzes exposed in urban areas. The compositions are given in weight percent.

	Composition of the alloy	Main types of corroded surfaces			
		Areas washed by the rainwater		Areas not washed by the rainwater	
		Pale green to blue (porous)	Black (compact, very hard)	Green (compact, ± hard)	"Opaque" black (hard)
Rodin's statues Paris [4] (1880-1920)	Cu (base) 3.6Sn 1.3Zn	mainly brochantite and cuprite (Sn/Cu = 0.8 ± 0.3)	brochantite, organic compounds (?) (Sn/Cu = 0.2 ± 0.1)	brochantite, gypsum, often antlerite, sometimes atacamite (Sn/Cu = 0.08 ± 0.07)	antlerite, gypsum, organic compounds (?), atacamite, brochantite (Sn/Cu = 0.02 ± 0.02)
Des Boers Quebec [5] (1905)	—	—	—	mainly brochantite, some atacamite and cuprite (Sn/Cu = 0.22)	brochantite, antlerite, atacamite, nantokite, cuprite, cassiterite (Sn/Cu = 0.014)
G.E. Cartier Quebec [5] (1920)	—	—	—	mainly brochantite, antlerite, cuprite and some atacamite (Sn/Cu = 0.25)	antlerite, brochantite, atacamite, nantokite, cuprite, cassiterite —
Mgr de Laval Quebec [5] (1908)	—	brochantite and cuprite (Sn/Cu = 1.56)	—	brochantite, cuprite (Sn/Cu = 0.24)	—
Le Triomphe de la Republique [6] Paris (1889)	88.4Cu, 4.3Sn, 5.3 Zn, 1.4Pb	mainly brochantite (Sn/Cu = 0.8 ± 0.3)	—	antlerite, brochantite, sometimes atacamite —	—
Stanislas Nancy (1831)	61Cu, 4Sn, 14.5Zn, 20Pb	brochantite, cuprite (Sn/Cu = 0.7 ± 0.1)	—	antlerite, quartz, gypsum, organic compounds? (Sn/Cu = 0.04 ± 0.03)	brochantite, quartz, organic compounds? (Sn/Cu = 0.01)

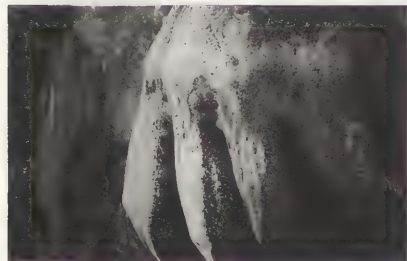


Figure 2. View of a bronze surface not exposed directly to the rain. The green compounds are partially recovered by "opaque" black crusts.

exposed to the rain. They are generally green deposits and/or opaque black crusts (3). These crusts (figure 2) contain various incorporated atmospheric particles and are often found above the green deposits. Compared to the first group, these corrosion compounds have a low or very low tin elemental content, and X-ray or IR spectrometry reveal that they contain both antlerite and brochantite.

Due to their amorphous nature, tin compounds are very difficult to identify with X-ray diffraction or infrared spectrometry. Variations in the colour or local composition of the compounds have not been considered in this work. They are not characteristics of the corrosion mechanism we will describe. Therefore, the red-brown or "quasi-metallic" grey surfaces or cupric oxide and organic compounds observed or detected will not be considered here (4).

Results given in Table I confirm that there is apparently no relationship between the exposure time and the nature of outermost corrosion layers. This can be correlated to a quasi-stationary state reached by the metallic materials in atmospheric conditions. The range of time to achieve this condition is decreasing: a bronze obtained its patina in several decades at the beginning of the century, while ten years seems to be actually sufficient in the urban areas of industrial countries (11). The results also confirm that although metallic structure relates directly to the alloy content, the Zn and Pb contents of the base alloy appear to have a minor influence on the main characteristics of the corrosion products (13).

These remarkably constant features reveal that outdoor bronzes have a general corrosion behaviour which is strongly dependent on the washing effect of rain-

water. Moreover, our understanding of corrosion phenomena must take into account the influence of the tin in the alloy. The nature of the outdoor bronze patinas cannot simply be regarded as that of the pure copper exposed to the atmospheric environment.

Qualitative model for patina formation

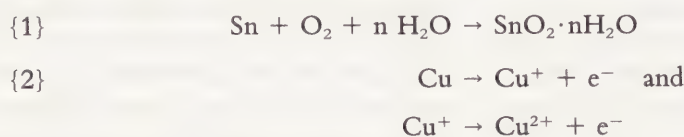
The observed physical and chemical characteristics of the bronze patinas have shown that some constant effects are observed. In order to explain these results, a qualitative model is proposed. This model is based on the formation process model of the corrosion structures observed for buried archaeological bronzes, according to the specific conditions of the atmospheric corrosion (14, 15).

The corrosion process is essentially caused by a presence of water on the bronze surface. The water on the surface results from precipitation (fog, rain, snow, etc.) or condensation at the metal surface (10, p. 756). In the absence of rainfall, the surface water can be assimilated into an electrolyte film whose composition and pH depend on the atmospheric compounds and the soluble corrosion products (9, p. 724). Atmospheric corrosion can be regarded as a corrosion process under an electrolyte film. So, by comparison with bronzes partially immersed in an aqueous electrolyte solution, two particularities must be recalled. First, the anodic dissolution products that cannot be evacuated from the surface can easily induce a deposit on the metal surface. This deposit may have either a protective effect if the products are insoluble and homogeneous, or an aggressive character if they are soluble and hygroscopic (i.e., porous). Secondly, the oxygen reduction rate is greater than that of the usual aqueous electrolyte at the initial stage of corrosion (11). Therefore, it appears that the presence of porous deposits has no protective effect. Moreover, these deposits can enhance the dissolution rate of the base alloy. This important point will be considered later in this paper.

Significant amounts of tin products are systematically detected in corrosion products on different bronzes. This result underlines the fact that the Cu-Sn alloy behaviour is more complex than that of the pure copper. Although copper is electrochemically more noble than tin, recent works have shown that for corrosive conditions, such as those of natural environments, the Cu-Sn corrosion behaviour is characterized by selective dissolution of the copper from the alpha phase of the alloy (14, 15). Copper species can form deposits on the surface, as previously mentioned. In relation to the effect of the rainfall, two types of surface evolutions must be distinguished.

Figure 3 is a schematic diagram of the corrosion process which results in the types of corrosion products described in the previous section. Three main steps are outlined.

The first step is the basic mechanism of the selective dissolution of copper. In contact with the surface water (electrolyte), the oxidation of the alloy can be represented as :



The "tin oxide," stable in aerated conditions and over a large pH range, is cathodic in comparison to the copper. The copper ions produced during the process may build a layer of copper compounds such as cuprous oxide on the top of the surface, while tin compounds remain in the internal part of the corrosion layer.

The second step of the process augments the thickness of the copper deposit by the formation of several copper II minerals, the nature of which is greatly dependent on the local atmospheric compositions, i.e., mainly brochantite in urban areas or chlorine-containing species in a marine environment. This process is similar to the formation of copper patinas discussed by Graedel (9, p. 736-

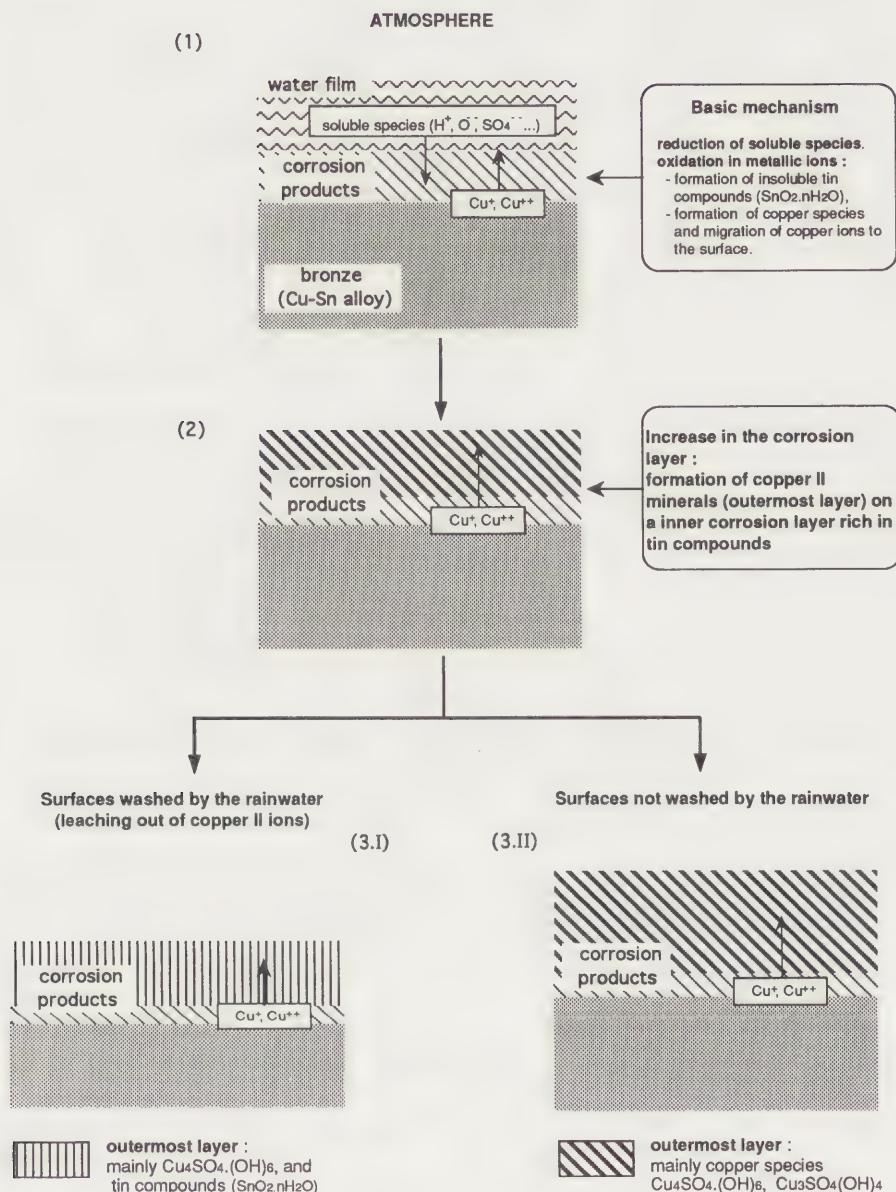


Figure 3. Schematic representation of the processes involved in the outdoor bronze corrosion.

738). For bronzes, the controlling step of the process is the migration of copper ions from the alloy to the atmosphere through the deposit.

The third step is related to the surface exposure conditions. For actual environments, the acidity of rain and smog can both solubilise the outermost copper corrosion compounds and promote the transformation of minerals. For example, brochantite is transformed into antlerite (this process will be discussed later in the paper). We can distinguish between surfaces directly washed by rainwater (step 3.I) and surfaces which are not exposed to rainfalls (step 3.II).

Soluble copper compounds are leached from the rain-exposed surface. The deposit described in the second step is progressively destroyed. The surface is "active" to the main corrosion process (i.e., selective dissolution of copper and internal oxidation of tin of the first step). The corrosion proceeds from a cyclic mechanism that is strongly correlated with the precipitation frequency. Then, the heterogeneities of the metallurgical structure locally enhance the formation of electrochemical coupling. The surface can be either anodic (pale green areas) or cathodic (islands of black compounds); this is probably related to the micro-segregations in the alloy.

The deposit of the deposit of copper species on surfaces protected from rainfall may be stable, but acidic waters can promote the transformation of brochantite

into antlerite (See fig. 3.II). Increasing the acidity of the water film (pH higher than 3.5) leads to the dissolution of brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) followed by antlerite precipitation ($\text{Cu}_3\text{SO}_4(\text{OH})_4$) in accordance with the reactions:



However, the antlerite formation needs an acidic water layer for a sufficiently long period of time (10, p. 765). In the case of short acidity periods, which do not allow the growth of antlerite, brochantite can reform on the surface. It is therefore expected that antlerite forms preferentially on the unexposed areas of sculptures that have lower evaporation rates than exposed surfaces.

The scenario developed here explains in a qualitative way nearly all of the results obtained on numerous outdoor bronzes. Nevertheless, this model does not permit one to solve all the problems. One of these problems is that the model is based on a phenomenological approach which can only be used to diagnose the degraded state but cannot predict the evolution of local patinas on outdoor monuments. The second point is that the exact process of the transition from Step 2 to Step 3.I is not clearly established. Finally, as mentioned by Gnedel, the nature and role of organic species could be very important, but these actors are not yet well understood (9, p. 739).

Application to the conservation of outdoor sculptures

Two main observations can be made based on the model described above. Both aged and recent bronze patinas are now less protective due to air pollution conditions in the environment. Also, the corrosion process is directly related to the presence of water on the metal surface.

Therefore, from the conservation point of view, two conclusions can be drawn. First, it is not relevant to remove the old patina to apply a new one, except to change the aesthetic appearance. Secondly, the conservation of outdoor bronze sculpture involves ensuring a good protection against exposure to water. To this end, conservation treatments may consist of cleaning, passivation, and coating.

Cleaning methods

What should we remove? Dust or "opaque" black surfaces, located on the non-exposed areas, must be removed first. These materials form a layer (sometimes more than 5 mm thick) that is very hygroscopic. Not only can these surfaces maintain a high humidity level on the alloy surface, but its black appearance is unaesthetic. Non-compact, pale green corrosion products located on the exposed area are very porous and hygroscopic, and can compromise coating adhesion by their pulverulence.

On the other hand, we can conserve black spots located on the exposed area that delineate the limit of the original surface. However, it is often necessary to remove them for their unaesthetic appearance. Green unexposed areas can be found under the "opaque" black layer. They are not always stable, as is revealed by the transformation of brochantite to antlerite, but they can be considered a good substrate for an applied protective coating.

Several methods have been used for cleaning outdoor bronze sculpture including manual cleaning (scalpel, metal brushes, etc.), electrically operated metal brushes, water pressure tools, water-abrasive, and air-abrasive techniques. Each method can often be used properly, but the most efficient in removal of dust and non-compact corrosion products is certainly the air abrasive method (16). By varying air pressure, the diameter of the nozzle, and the nature of the abrasive (softness, size, geometry), it is possible to obtain a very good small- and large-scale cleaning. The walnut shell air-abrasive technique (See figure 4) is widely used for bronze cleaning without stripping (17).



Figure 4. Cleaning of a bronze statue by walnut shells with an air-abrasive technique.

Passivation

There are few corrosion inhibitors available for bronze. Authors have only considered the role of copper and have mentioned the utilisation of benzo-

triazole (BTA), a copper corrosion inhibitor for outdoor bronze. Is benzotriazole a good inhibitor for bronze?

There is much to support the use of BTA in the literature. Benzotriazole may build up a three dimensional film with copper, protecting the alloy from outside attack. Turgoose shows that the formation of this film on ancient artifacts happened after a week of immersion in an alcohol bath; obviously, this is not possible for outdoor bronzes (18).

Benzotriazole has also been added to such coating systems as microcrystalline wax formulations to increase their quality, such as in microcrystalline wax. For some time, BTA was also added to the famous acrylic resin called Incralac (19, 20).

Coatings

Acrylic, polyester, polyurethane, natural wax, and mineral wax have been used as coatings for outdoor bronzes. The characteristics to consider when selecting as coating are life-time, reversibility, aesthetic appearance, and facility of maintenance.

Each chemical family has very different products and it is very difficult to give general recommendations. However, polyurethane can be considered as the best for its life-time (10 years), but it is also the worst for reversibility and facility of maintenance, as it requires complete removal by air-abrasive methods and reapplication for adequate protection. Mineral waxes (microcrystalline) have short lifetimes (2 to 5 years), but have excellent reversibility and maintenance properties. For instance, maintenance consists of a simple water cleaning and application of a new layer. Acrylic has intermediate properties, with a relatively good lifetime, and quite good solvent-reversibility properties (20). It is noteworthy that natural wax can generate acid radicals which increases corrosivity at the surface. None of the coatings are fully convenient, but our choice is oriented to the use of a microcrystalline wax (See figure 5) with a high melting point because of its facility of maintenance. A two years' maintenance is also good, because it forces people to maintain and to clean their sculptures. Whatever cleaning technique and protection system is chosen, we must be able to understand what should we remove, what should we protect, how much time the coating can be protective, and what is the maintenance process.



Figure 5. Coating of a bronze statue by applying microcrystalline wax on the cleaned surface.

Conclusion

The corrosion behaviour of Cu-Sn alloys in outdoor atmospheric conditions is notably more complex than for the pure copper. Though copper is intrinsically a more noble metal than tin, the analysis of corrosion products revealed a tin enrichment; this relates to the formation of tin oxide, which is cathodic to copper. This phenomenon is always observed for bronze corrosion and is attributed to a selective dissolution of copper from the Cu-Sn alloy. If the copper compounds (mainly cuprous oxide and hydroxysulfates) can build a protective and adherent deposit on the surface, the dissolution of the alloy will be stopped. If such a deposit cannot be built up, i.e., for areas washed by rainwater, the copper compounds will be leached and the corrosion will proceed by a cyclic mechanism strongly related to the frequency of rainfall.

A new framework is given in this work for understanding the formation of natural patinas. It enables future research to determine the precise mechanism of the destabilisation of the copper compound layers and to improve conservation treatments.

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Abstract

The following six treatment methods were used to stabilize iron excavated from a wet land site at Red Bay, Labrador: alkaline sulfite, ethylene diamine, electrolysis, hot washing, dewatering, and no treatment. Most of this iron was treated before 1985. In May 1991, a survey of the present condition of 2,163 treated iron artifacts was carried out to evaluate the effectiveness of the different treatment methods. Visual inspection was used to classify the iron as "stable" if it had a uniform surface appearance, or "unstable" if it showed evidence of active corrosion. Results from this survey are presented. Treatments by alkaline sulfite, ethylene diamine, and electrolysis were successful in stabilizing Red Bay iron. Hot washing, dewatering, or leaving the artifacts untreated were not successful in stabilizing the iron.

Keywords

Iron, archaeological, treatments, alkaline sulfite, ethylene diamine, electrolysis, hot wash

Stability of Treated Iron: A Comparison of Treatment Methods

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Introduction

Since 1978, the Canadian Conservation Institute (CCI) has been providing conservation advice and services to archaeologists at the Memorial University of Newfoundland in St. John's, Newfoundland, for artifacts excavated from a coastal land site at Red Bay, Labrador. The artifacts date from the occupation of Red Bay between about A.D. 1550 and A.D. 1600 by Basque whalers from the Bay of Biscay in Spain and France. The whalers sailed to Red Bay during the summer months to hunt whales and render oil from the blubber. This oil, sold in Europe, was used mainly for lighting and soap making, as a lubricant, and in the cloth and leather industries.[1]

The artifacts were recovered from a wet, saline burial environment that tended to be acidic because of the surrounding peat bogs. Excavated artifacts included several thousand iron objects. Their condition varied widely, from very robust to totally corroded. In most cases, the original shapes of the objects were preserved in the corrosion layer, so the loss of this layer would have resulted in the loss of this information. One of the problems that had to be overcome was the shortage of conservation facilities; although CCI could provide some treatment services, it could not treat the thousands of fragments of nails and other objects excavated each summer.

Between 1979 and 1981, various treatments were carried out at CCI to determine the most effective and practical way to treat these objects in bulk using the facilities and personnel at Memorial University.[2] One method attempted in the field lab in 1980 was to dewater a selected group of nails using a commercial dewatering compound called "Ferromede." It was recognized at the time that this would not prevent active corrosion in iron contaminated by chloride ions, but it was hoped that the rate of corrosion would be slowed down by this treatment.

After assessing the conservation requirements of the objects, a decision was made to keep all the iron objects wet until a conclusion regarding their conservation could be reached. Most of the artifacts were wrought iron nails, presumably used for the construction of the tryworks and other wooden structures. Other iron objects included barbed iron harpoons, ferrules, knives, and cooper's tools. All the objects were x-radiographed in the field, and were stored in deionized water for shipping either to Memorial University or to CCI. Objects sent to CCI included composite artifacts and recognizable objects other than nails. Memorial University received the majority of the iron, which amounted to several thousand nails over the twelve years of excavation.

After treatment at CCI, the iron and other artifacts from Red Bay were sent to the Archaeology Unit at Memorial University for storage. The artifacts are stored in drawers in well-sealed metal specimen cases (Lane cases) in a room with an uncontrolled environment. Lane cases offer optimum protection from incidents of high humidity since the doors in the cases make a good seal with the cabinet frame. Silica gel has been placed inside each drawer to maintain as low a relative humidity as possible. Also, the drawers are lined with either acid-free tissue paper or ethafoam. These storage cabinets are located in a room where the temperature is reasonably stable at $19^{\circ}\text{C} \pm 2^{\circ}\text{C}$, although in the middle of summer, the temperature can reach 26°C during the afternoon. There are large fluctuations in relative humidity, ranging from as low as 25% during the winter

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to between 80% and 100% during the summer and fall. These are not unusual conditions for buildings in a coastal environment.

Survey techniques

In May 1991, the condition of treated iron from Red Bay that was being stored at Memorial University was surveyed. A similar survey had been done in May 1985.[3] The iron's condition was recorded on a master list containing the catalogue numbers of iron artifacts that had been dewatered in the field in 1980 or that had been treated at CCI.

We did not survey the condition of the several thousand nails from the same site that had been treated at Memorial University. The technique used for the majority of the nails was long-term storage in 1% w/v sodium hydroxide, followed by mechanical cleaning, then hot washing to remove residual sodium hydroxide. The success of this method has yet to be assessed, but at present, this technique appears to be practical for bulk treatment of iron.[4]

A visual technique was used for classifying the condition of the iron as either stable or unstable. Iron with a surface that was either uniformly rusted or uniformly colored by a coating of tannic acid or wax was considered to be stable. Unstable iron was recognized by the presence of either surface sweating or akaganéite (β -FeOOH).[5] Surface sweating (weeping) is defined as the formation of yellow, brown, or orange droplets when the relative humidity is above about 70%, or the formation of similarly colored blisters from the desiccation of sweating iron. Akaganéite appears as long, thin, orange crystals that form at the metal/corrosion interface. The crystals have a fuzzy appearance. Cracks in the outer layer of corrosion are often the first indication that akaganéite is present.

Iron conservation treatments

In 1978, when the excavations at Red Bay first generated large quantities of iron artifacts, appropriate conservation treatments had to be investigated and a systematic treatment approach had to be developed. It was recognized, however, that chlorides had to be removed from the iron—especially if a core of solid iron was present—to prevent active corrosion that causes iron to disintegrate. As a result of CCI's investigations, the following six conservation treatments were used.

1. Alkaline sulfite: This treatment was used as described by North and Pearson, but without the post-treatment use of a barium hydroxide rinse.[6] Prior to treatment, the iron was stored in 1% w/v sodium hydroxide. During treatment, batches of iron were washed in sealed containers of a hot solution (60°C) of 0.5 M sodium hydroxide (NaOH) and 0.5 M sodium sulfite (Na_2SO_3). The solution was changed whenever the chloride levels became constant, and the treatment was stopped when chlorides could no longer be detected. Quantitative chloride levels were monitored using an ion-specific electrode.[7] To remove residual chemicals after treatment, the iron was washed in a series of hot deionized water baths (either boiling or heated to between 50°C and 60°C) until a neutral pH was reached. Finally, the artifacts were dewatered with acetone and coated with tannic acid.
2. Dewatering: In 1980, approximately 700 iron objects were dried by removing water (dewatering) with a commercial product called Ferromede (probably Ferromede 360). This was done either immediately after the objects were excavated or after they had been stored in 1% w/v sodium hydroxide. This commercial product was designed to displace water from a clean metal surface and leave behind a protective film of waxes and oils. It was purchased from S.A.C. of Canada Ltd., Toronto, Ontario. (At present, it is no longer available in North America.) If objects had been stored in sodium hydroxide, they were rinsed with deionized water before soaking in Ferromede for about one day, and were air-dried. If objects were freshly excavated, they were immersed in Ferromede and air-dried.
3. Electrolysis: Iron objects containing a substantial iron core were treated by electrolysis. The iron object was the cathode, stainless steel plates were the

anodes, and the electrolyte was 1% w/v sodium hydroxide. Chloride levels were monitored quantitatively with the ion-specific electrode mentioned above to determine when the treatment was finished. After treatment, the iron was hot washed in successive baths of deionized water (which either was boiling or had been heated to between 50° and 60°C) until a neutral pH was obtained, dewatered with acetone, and coated with either tannic acid or wax.

4. Ethylene diamine: After being stored in 2% w/v sodium hydroxide, iron artifacts were treated by exposing them to an aqueous solution of ethylene diamine. This treatment was developed by James Argo in 1981 in response to the need to treat archaeological iron from Red Bay.[8] During the initial development of the treatment, iron was suspended over boiling aqueous 20% v/v ethylene diamine. The solution was changed daily until low chloride readings (less than 20 ppm) were obtained. Later, the procedure was changed so that the iron was immersed in 5% v/v ethylene diamine heated to about 50°C during the day and cooled overnight. The solution was changed whenever the chloride levels became constant, and the treatment was stopped when a low chloride level was reached. Chloride levels were monitored using the same method as for alkaline sulfite. Following treatment, the iron was hot washed in deionized water that either was boiling or that had been heated to between 50°C and 60°C to remove excess ethylene diamine, dewatered with acetone, and coated with tannic acid.

5. Hot wash: A limited number of iron artifacts were hot washed by boiling them in successive baths of deionized water until no chloride ions could be detected in the water over a period of several weeks. The chloride levels were monitored daily using a qualitative silver nitrate test.[9] Following treatment, the objects were dewatered with acetone and coated with tannic acid.

6. No treatment: A few pieces of iron excavated in poor condition around 1980 were not treated; they were simply allowed to dry.

Survey results and discussion

A total of 2,163 iron objects were surveyed. Of these, about 90% were treated and returned to Memorial University before 1985. Table I groups the results of the 1991 survey according to treatment and according to whether the objects were stable or unstable. The unstable categories contain 11 objects identified as "disintegrated" on their treatment records. The records at Memorial University were not searched for objects that had disintegrated during storage. Also included in Table I are the results from the 1985 survey. [3]

Table I. Results from the 1991 survey of Red Bay iron at the Memorial University of Newfoundland. Results from the 1985 survey are also included. [3]

Treatment	Total iron 1991	Total unstable 1991	Percent unstable 1991	Total iron 1985	Percent unstable 1985
Alkaline sulfite	438	1	0.2%	475	1%
Ethylene diamine	857	30	3.5%	484	4%
Electrolysis	100	17	17.0%	33	0%
No treatment	24	5	20.8%	26	19%
Dewatered	700	299	42.7%	778	42%
Hot wash	44	30	68.2%	44	71%

Although the alkaline sulfite treatment has not been used since 1980, it has proved to be very effective in stabilizing Red Bay iron. Only 0.2% of the 438 treated iron objects were unstable in 1991, which is similar to the reported 1% unstable in 1985. This treatment was discontinued after 1980 because objects were porous and, therefore, tended to be very fragile after treatment. Wrought iron nails became mushy and hard to handle, and many artifacts needed consolidation after treatment, especially if they had broken during treatment. Objects that survived this harsh chemical treatment with the least damage were those with a significant amount of iron.

A total of 857 iron objects had been treated with ethylene diamine by 1991, with 85% of these treated before the end of 1985. In 1991, only 3.5% of these objects were unstable, a similar result to the 4% unstable observed in 1985. It is a very good treatment for heavily corroded iron, and it is still being used today by conservators at CCI. The difference in the results between alkaline sulfite and ethylene diamine might be attributed to the fact that alkaline sulfite is not an appropriate treatment if it is important to retain thick layers of corrosion. Table II contains results from a further breakdown of the ethylene diamine treatment on the basis of whether iron was treated by refluxing or by immersion. Also included in this table are objects treated by both refluxing and immersion. The numerical differences between refluxing or immersion are not significant.

Table II. Stability of artifacts from the 1991 iron survey that were treated by different methods that used ethylene diamine.

Treatment	Total number	Percent unstable
Refluxing	261	3.8%
Immersion	548	2.9%
Refluxing & immersion	26	3.8%

Electrolysis has been used on 20 or fewer artifacts each year. Artifacts usually chosen for treatment by electrolysis were ones in relatively good condition with a large amount of metal remaining. No unstable objects were noted during the 1985 survey of 33 iron artifacts treated by electrolysis. From this group of 33 objects, 25 were in storage at Memorial University in 1991, and of these 25, only two were unstable. This corresponds to 8% unstable. Of the 100 iron pieces treated by electrolysis by 1991, 17.0% were unstable.

One contribution to this high percentage of unstable iron treated by electrolysis may have been one batch of at least 20 iron pieces. Electrolysis of this batch was probably stopped too early, because 30% are now unstable. If the results from these 20 pieces are removed from the total, the percentage unstable drops to 13.8%. Although chloride levels had reached an acceptably low level before treatment was stopped, this level may not have accurately reflected the chloride levels of some of the pieces.

Of the 24 iron objects not treated, 20.8% were unstable in 1991. This result is similar to the 19% found to be unstable in 1985. It is likely that much of the untreated iron excavated around 1980 may have already disintegrated. Those surviving until 1991 are likely to be highly mineralized and, therefore, unlikely to suffer rapid deterioration.

In 1991, out of a total of 700 iron objects that had been dewatered (mainly with Ferromede), 42.7% were unstable. This is similar to the 42% unstable in 1985. Thus, over half of these iron objects are still stable and are available for study purposes. In 1980, the dewatering of large quantities of iron with Ferromede was an attempt to retard the deterioration of the iron artifacts so that archaeologists would have a period of one to two years to study them. It was never expected that this treatment would stabilize the iron for longer periods of time. An additional study of these dewatered pieces was carried out at Memorial University in 1991. All dewatered objects were weighed. Unstable objects were on average heavier, with an average weight of 14 grams per object, than the stable objects, with an average weight of 5 grams per object. These dewatered objects probably contain a significant amount of chloride ions, because dewatering with Ferromede was not intended as a method for removing chlorides. Since chlorides cause active corrosion only when there is iron left to corrode, this correlation of heavier objects being unstable and lighter objects being stable was to be expected.[10]

The 44 hot-washed iron objects were treated before the end of 1980. By 1991, 68.2% of these were unstable. This is similar to the 71% observed in 1985. Even though there is only a statistically small set of hot-washed objects, these results confirm what was recognized earlier—that this treatment is not appropriate for removing chlorides from iron.

Conclusions

Results have been presented from a survey of the present condition of 2,163 iron artifacts excavated from an archaeological site in Red Bay, Labrador and treated by one of six methods. The majority of this iron was treated before the end of 1985.

Alkaline sulfite, ethylene diamine, and electrolysis are treatments that have been successful in stabilizing this Red Bay iron. The alkaline sulfite treatment was the most successful method, with 99.8% of the treated objects still stable in 1991. The ethylene diamine treatment was almost as successful, with 96.5% of the treated objects still stable. Electrolysis was not quite so successful in stabilizing iron, with 83% still stable. Hot washing, dewatering, and no treatment are methods that were not successful in stabilizing the Red Bay iron.

Acknowledgements

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Working Group 23

Icons

Icônes



Abstract

A conservation treatment of 17th century appliqué fabric icons was developed based upon the results of examination of their technology, materials, and condition.

Keywords

Icon, appliqué, fabrics, cleaning, consolidation

The Conservation of Fabrics on Icons Produced by the Appliqué Technique

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Technique of appliqué fabric

An icon stand executed in the technique of appliqué fabric belongs to the tower Crucifix Church of the Grand Palace in the Moscow Kremlin. The icon stand was produced by the czar's icon painters V. Poznansky, I. Bezmyan, and B. Saltanov (1). The flesh paint and some other fragments were painted in oil on canvas. The background, vestments, and some other fragments were painted in oil on canvas fabric. The background, vestments, and decorative elements were glued on the wooden support as well as the painted details.

The costly satin, velvet, brocades, and rep fabrics brought to Russia in the 17th century were used to produce appliqué. These fabrics have various colours; one can see at least 16 colours of satin and nine colours of reps. Their graphic design also varies from large patterns to small rapporté. The fabrics are also adorned with bands, tapes, laces, and silver and gilt papers. The bands and tapes are located along the edges of the icons. The lace marks the folds of the vestments and some other details, and the papers are used for the inscriptions, adornments, and fragments of decorum. Some icons bear fabrics glued along the outlines of the image drawn on the wooden support, while others have appliqué fabric lined on paper, with preparatory drawings glued to the wooden support.

Condition of the appliqué icon

In the course of time since the icons were made, the surface of the fabric became soiled with dust and soot. One can see spots of extruded wax and glue, and some dyes have faded away. Some areas of the surface show such condition details as lace or band removal, slight losses, cuts, and removal of fabric that look like swellings.

Research

Research was carried out to select the correct method to conserve the appliqué fabrics. Microscopic analysis of the fibers with polarized light showed that their condition was satisfactory, and that their structure was stable. The dyes were examined using polarized light microscopy, spectrophotometry, and thin-layer chromatography. The results of these tests showed that organic natural dyes were used according to the classic technology of vat and mordant dyeing. The red fabrics were coloured with cochineal, while violet-coloured fabrics were dyed with an indigo-cochineal combination. The green hues were produced by use of two dyes: blue vat indigo and yellow mordant dyes of the flavone type, one of which was mignonette. Samples of glue that had been used to adhere the appliqué fabrics to the icons were identified using optical microscopy and infrared spectroscopy (IR). The IR results identified these samples as gelatine (probably fish glue), though some glue samples also included flour paste.

Treatment

The method of the cleaning and consolidation treatment of the appliqué fabrics was developed based on the results of examination. When removal of dust and spots had been carried out, we resorted to an aqueous method to remove the surface dirt, using swabs moistened with 30–40°C distilled water. To clean the badly soiled areas of the fabrics, we used a mixture of water, ethyl alcohol, and glycerine (100ml, 5–10g, and 0.5–1g, respectively). After cleaning, the moisture and soiling were removed using filter paper. The cleaning was effective, and the use of ethyl alcohol and glycerine softened the desiccated fibers.

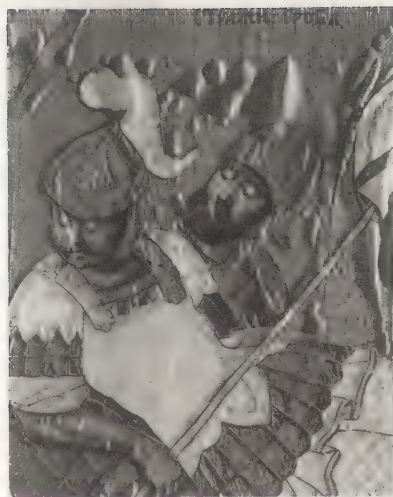


Figure 1. *The Resurrection*, before conservation.



Figure 2. *The Resurrection*, after conservation.



Figure 3. Cleaning procedure.

A special feature of the conservation of the appliqué fabric was a consolidation treatment of the moistened areas of the fabric; this step was performed immediately after cleaning. The consolidation paste was a 6% solution of flour paste (2). The paste was injected or applied by brush; a weight (0.3–1kg) was applied to the surface, as necessary.

Conclusion

In summary, the method used to conserve the appliqué fabrics on icons produced in the 17th century involved traditional Russian methods used for more than 100 years: aqueous cleaning and consolidation of the fabric using flour paste. The icon-stand conserved five years ago is still in good condition.

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Abstract

This paper introduces a new approach to the conservation of Byzantine icons with the use of radiodiagnostic equipment commonly found in hospitals. Three examples are provided that demonstrate the utility of this method.

Keywords

Radiography, conservation, Byzantine icons



Figure 1. *Panagia the Hodegetria*.



Figure 2. X-radiogram of *Panagia the Hodegetria*.

The Contribution of Radiodiagnostic Hospital Equipment in the Conservation of Byzantine Icons

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Introduction

It is strongly recommended that before any restoration of a Byzantine icon be attempted, a thorough series of tests should be performed (1, 2). For this purpose, various methods have been developed such as infra-red photography, ultraviolet photography, electron microprobe analysis, X-ray examination, etc. All these methods provide the conservator with valuable information about the object to be restored.

Background

X-ray radiography is one of the oldest methods used in trying to determine the answer to the question of how a particular icon was painted. It provides information concerning the canvas support, ground layer, wood support, wood worm tunnels, nails, paint layers, and underlying painting. Radiography also serves as an identifying document for the painting. No one can reproduce an icon that results in the same radiogram as the original (3).

Greece is blessed with a large number of icons dating from the 10th to the 14th century that are spread throughout the country. The constant use of icons within the church and their constant retouching leads to their alteration, not only on the actual painting surface but on its substructure as well. For the restorer, the information provided by radiography allows him to understand the history of the icon and the trends in painting styles and techniques, as well as any previous restoration attempts. The study of the layers on even one icon brings to life its history and leaves the art historian breathless.

X-radiography is an invaluable tool for the restorer of Byzantine icons. Specialized X-ray equipment produces the grenz rays which can be easily absorbed by works of art. The main feature of this specialized equipment is a tubehead that has a beryllium window. To produce radiograms of maximum quality, a long exposure time is required, longer than the four second exposure time of standard medical radiodiagnostic units. The main disadvantage of the specialized equipment is its high cost; to justify the expense, the equipment must be used continuously, which demands constant maintenance and replenishment of its chemicals. For these reasons, only larger laboratories can afford this equipment.

The necessity of using radiography has led us to develop a means by which the investigation of Byzantine icons can be accomplished by using common radiodiagnostic equipment.

Description of the method

All types of radiodiagnostic equipment have the problem of short exposure times. To solve this problem, a multiple exposure technique was developed.

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Figure 3. Traces of silver revetments visible after their removal from the icon, *Panagia the Triherousa*.



Figure 4. X-radiogram of *Panagia the Triherousa*, revealing traces of the Child's clothing where the third silver hand is attached.

This technique is widely used for creating special effects photography. In our case, taking multiple shots of the same icon from a set distance achieves a long exposure time, since the total exposure time is the sum of all partial times.

Forty-five successful radiograms were taken during the development and perfection of this method. Their data were as follows: kilovoltage 32–40 KV, milliamperage 160–300 mA, and total exposure time 9–16 seconds. The exposure time was achieved by shooting the icon three or four times with a duration of three or four seconds.

To obtain radiograms with the desired geometric degree of sharpness, the instructions given in the bibliography were followed (4). The focal/film and focal/object distance was near 1.0 m. The focal spot size was kept to 0.6, the minimum available. In order to keep the object/film distance to a minimum, the icons were placed on the table of the X-ray machine with the painted surface face down. Elastic material, placed underneath, pressed the film to the icon, enabling full contact.

The film type was AGFA GEVAERT Structurix D6RDW. It is double coated with a fine emulsion for a more detailed radiogram with dimensions of 0.34×0.43 m. It requires 90 seconds for development using a common automatic processing machine of the deep tank type.

Application of the method

The method was applied to three icons: *Panagia the Hodegetria*, *Panagia the Triherousa* (The Three-Handed Virgin), and *Archon Michael* (Archangel Michael).

The dimensions of the icon, *Panagia the Hodegetria*, are 0.29×0.36 m (See fig. 1). It has a wood support with a thick paper covering. An image of the Panagia (Virgin Mary) is painted on the paper. It is dated to the early 20th century and has a primitive style. Radiography revealed that an original painting lay beneath the visible one (See fig. 2). The original is an icon of high artistic quality dated to the 16th century, made by a skilled master of the Cretan school. The radiogram captures the image of the original icon clearly and with good detail. Of the paper icon on the surface, only the Virgin's eyes and the child's head appear. (This occurs because of the low absorption of x-rays by the organic pigments widely used by icon painters in the early 20th century.) The radiogram also reveals the painter's personal style, particularly his sensitivity to the delicate modelling of the body and face.

The *Panagia the Triherousa* icon is of the intercessory type with dimensions of 0.60×1.14 m and is dated to the 15th century. A thick coat of oxidized varnish and dirt completely obscured the painting. Silver revetments covered the aureoles and the hands of both Mother and Child, adding an extra silver hand just below the original right hand of the Virgin.

This occurred in accordance with the traditional name of the *Three-Handed Virgin* in its traditional position; we find the third hand in exactly the same place in all other examples of three-handed Virgins. The traces of silver revetments are clearly visible even after their removal (See fig. 3). Radiography revealed many secrets of the icon. For example, a cogged aureole was painted by a later icon painter. Also, the inscription H MEΣITPIA (The Mesitria) was revealed. The most surprising discovery was that no third hand was painted on the original icon. The radiogram reveals that traces of the Child's clothing are present in the place where the third hand was painted (See fig. 4). A photograph of the icon after cleaning is provided (See fig. 5).

The dimensions of the icon, *Archon Michael*, are 0.70×0.40 m and it dates from the 18th century. The icon shows Archangel Michael holding the soul of an old dead man while below Satan tries to pull the soul into Hell (See fig. 6). A detail of the area around the soul is given (See fig. 7). One discovery among others revealed by the radiogram was an older depiction of the soul beneath the ground layer (See fig. 8). A detail of both depictions of the soul are given (See fig. 9).



Figure 5. Photograph of *Panagia the Triherousa*, after cleaning.



Figure 6. *Archon Michael* (Archangel Michael).



Figure 7. A detail of *Archon Michael*, showing the area around the soul of the dead man.

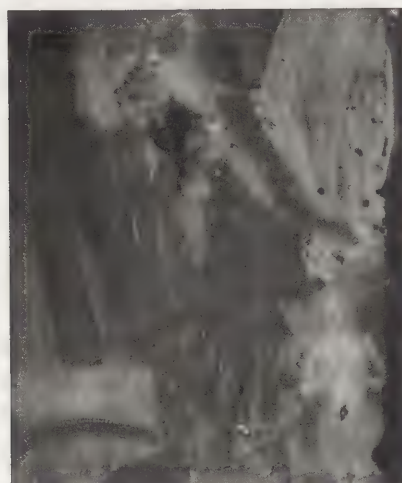


Figure 8. X-radiogram of *Archon Michael*, showing an earlier depiction of the soul.



Figure 9. A detail of both depictions of the soul.

Conclusion

The multiple exposure method is a valuable tool for the restoration laboratory that cannot afford specialized X-ray equipment. Furthermore, the three examples above demonstrate that any attempt to restore Byzantine icons should begin with an X-ray examination to avoid overlooking or destroying important information.

Acknowledgements

This work is dedicated to our teacher of conservation, Mr. Stavros Baltoyannis, former Inspector of Conservation at the Greek Ministry of Culture. The authors would also like

to express their warm thanks to the staff of the Agios Demetrios Hospital for their generous service during the development of this method.

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Abstract

In the 1920s and 1930s, several iconostases were disassembled and the icons were distributed among several museums throughout Russia. When the iconostases were later reunited, the differences in appearance of the individual icons were striking. This was largely the result of the various conservation treatments that each unit had undergone. This article argues for a unified approach to the conservation of all icons in a given iconostasis.

Keywords

Icon, iconostasis, conservation, Russia

Conservation Treatment of Icons from an Iconostasis

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Groups of icons that are part of disassembled iconostases are included in the collections of various Russian museums. The oldest examples date from the 15th century. During the 1920s and 1930s, several iconostases were taken apart and the pieces were distributed among several different museums throughout the country. Some of the iconostases that suffered this fate include one painted by Andrei Rublev for the Cathedral of the Assumption in the city of Vladimir, one painted in 1497 for the Cathedral of the Assumption in the Kirillo-Belozerskij Monastery, and one painted by Dionysos in the 1490s for the Therapontos Cloister. The icons belonging to these iconostases underwent different conservation treatments by different specialists at different times. No consideration was given to their common origin and, therefore, no unified approach was taken to such common problems as losses on the original paint layer. When the iconostases were reunited, usually at special exhibitions, the disparity in the appearance of the various icons was striking, particularly since they were all originally from the brush of one master.

Later, the practice of separating icons from one iconostasis ended, and iconostases began to be treated as a whole. Very few icons are now treated in isolation, even when they are only given preventive conservation treatment. In addition, icons from a single iconostasis are no longer dispersed throughout many museums. Instead, they are kept together in a single repository where it is possible to carry out the unified conservation treatments that are such an important part of the project under discussion.

Dozens of iconostases dating from the 16th to 18th centuries—many hundreds of icons in total—have undergone conservation treatment at the Inter-Regional Scientific and Conservation Artistic Department in Moscow.

The iconostases from the 16th century that we have treated include ones from the Cathedral of the St. Antonios Dymsky Monastery, from the Church of Saints Peter and Paul at Kozhevniky in Novgorod (dating from the late 1500s), from the Cathedral of the Assumption and the Church of the Holy Trinity in Savvazhsk (dating from the late 1500s), and from the Church of the Transfiguration in the Kirill Belozerskij Monastery on Novy Lake (dating from 1597). These iconostases, which include several hundred icons, occupy a special position among the ensembles: having undergone professional conservation treatment, these iconostases have broadened investigators' knowledge of the artistic style during the era of Ivan the Terrible.

Another group of iconostases that have been restored by our Department was created during the 17th century by the leading icon painters of the Czars. Particularly noteworthy are iconostases from the Churches in the Kremlin dedicated to the Miracle of Honae and to the Ascension, Moscow's Church of the Protection of Our Lady in Filae, and the Stroganov family's church in Niznyj Novgorod. These works were likely produced by such well-known Czarist icon painters as Kirril Ulyanov, Karp Zolotarev, and Fedor Zubov.

A third group of iconostases dates from the late 17th and early 18th centuries, and demonstrates the variety of artistic trends in the Russian province at that time. Included among this group are iconostases from the Cathedral dedicated to the Archangel Michael; from the Churches of St. Demetrios of Thessaloniki and the Church of the Ascension, both in Veliki Ustjug; and from the Church of St. Nicholas of Myra in Vysokij Ostrov in the Novgorod region.

Our experience has shown that a unified method of treating these iconostases has a number of obvious advantages. Given that all parts of a given iconostasis have been exposed to the same conditions in a church or a museum and that

all the icons have a common technical history and technological base, all the factors suggest the use of an integrated approach to conservation treatment. A single team, led by the most experienced conservator, carries out the entire treatment. Treatments are tested on two or three icons by experienced specialists in the Department, and then are applied to the rest of the ensemble. Applying the same conservation procedures to a number of icons allows us to address such methodological problems as devising an integral approach to paint losses and recommending ideal conditions for exhibiting the icons. When the icons are returned to the church that has the framework of the iconostasis, a specialized team of carvers and gilders works in situ and maintains close contact with the conservators who will continue to care for the iconostasis.

Using this unified approach, we can preserve the artistic integrity of iconostases as they were conceived by the artists who created them.

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A bibliography in Russian is available from the author.

Working Group 24

Rock Art

Art rupestre



Abstract

The Cerro Intihuasi, near the city of Río Cuarto, Córdoba, Argentina, is one of the best known rock painting sites. There are five decorated shelters in the granitoid blocks that form the top of this hill. The main deterioration problem was found to be water seepage through microfissures in the rock. The paper describes experimental "rain" events used to measure the percolation pattern through one of the shelters. Possible solutions to protect this site, such as revegetation and constructing a cover for the roof of the shelter, are discussed.

Keywords

Rock painting, rock art, shelter, pre-Columbian art, Cerro Intihuasi, stone deterioration, water seepage, site protection

The Rock Art at Cerro Intihuasi, Córdoba, Argentina: Deterioration of the Stone Support

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Introduction

The Cerro Intihuasi lies some 50 kilometers to the west of the city Río Cuarto in the province of Córdoba, Argentina. It has a height of about 800 m, and on the southwest slope there are five natural shelters. These shelters have been decorated with rock art by the Comechingones Indians who lived in the area. Radiocarbon dating of residues found in a hearth, found at some 70 cm depth during an excavation in one of these shelters, gave an age of 780 years B.P. (± 100 years), i.e., 11th to 12th century, to the occupation of these sites (1).

The paintings, mainly done with white pigment, show ensemble scenes, such as long lines of "ñandúes," American ostriches (*Rhea americana*) with their wings open, ambushing pumas, Indians with bows and arrows, and abstract drawings forming ornamental bands. All drawings were carried out with extreme simplicity.

The entire area of central Córdoba is rich in archaeological sites, the Cerro Intihuasi being one of the best known sites (2). The preservation of this representative site of pre-Columbian rock art requires a detailed study of the deterioration causes that affect it. Of these, the movement of water through the rock has been identified as one of the main causes of deterioration (3). The present paper presents the results obtained in tests carried out at one of the sites. Tests were performed to better understand the water migration through the rock as well as relative humidity and moisture condensation problems.

Site description

The Intihuasi hill is formed by a series of outcrops elongated in the NNW-SSE direction. The five decorated shelters are found on each of five roughly rectangular blocks, some 50 m below and slightly west of the top. The blocks are separated by narrow diaclasses that range from 10 cm to 1 m in width, and are presently filled with accumulated debris, stones, and humus. The shelters formed through natural weathering and several other overhangs can be found in the area. A more detailed description of these sites is described elsewhere (3).

The shelter studied in more detail and reported here is called IW1. Figures 1a and 1b show a cross section and a front view of the shelter, respectively. The height to the overhang is 1.9 m. The tip of the overhang is about 7 cm thick and extends approximately 1 m into the area where the drawings begin. The depth is about 3.5 m.

The shelter has a large overhang that protects the paintings from direct rain. The edge of the overhang forms a water drip line, except in two areas where water washes directly down the rock.

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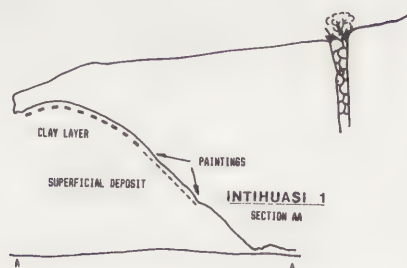


Figure 1a. Cross section of shelter IW1, Cerro Intihuasi.

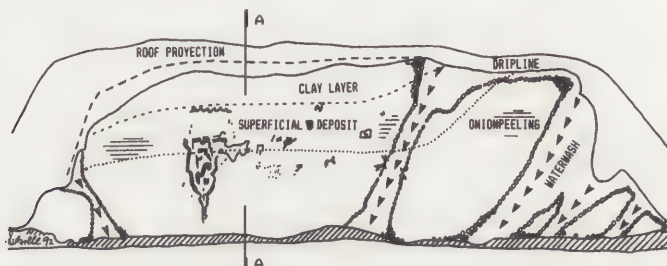


Figure 1b. Front view of shelter IW1, Cerro Intihuasi.

The internal wall of the shelter has a relatively "sound" rock surface, of greyish-white pink colour and medium-coarse grains, and is fairly solid. No concretions or deposits are visible to the naked eye. In some areas deep flaking and onion peeling is apparent. These flaking areas increase in depth towards the top of the shelter. The thickness of the layers ranges from a few millimeters to one centimeter; the space between them is usually filled by clay-like material. The location of these areas may indicate that they are caused by soluble salts migrating from the wet waterwash. The nature of these salts is yet to be established.

The vault of the shelter has a 0.5 cm-thick layer of clays deposited on it. This deposit of reddish-brown color has a fine and smooth texture and can be removed easily by brushing. The bottom end of the layer is located at about 1.7 m from the base of the shelter. It is interesting to note that this is the height reached by direct sunlight during the autumn and spring equinoxes, and slightly above in summer, confirming the importance that illumination has on the drying processes occurring in the shelter.

Underneath this clay layer is a similar deposit some 60 cm wide. This brown deposit adheres firmly to the support and is also found on both sides of the waterwash. The brown deposit is a mixture of grains and clays cemented together and to the support. This adherent layer partly covers some painted motifs. Figure 2 shows the appearance of this deposit under the scanning electron microscope.

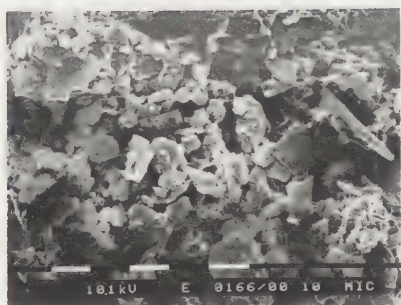


Figure 2. SEM photomicrograph showing the closely arranged clay and mineral particles in the brownish deposit along the waterwash.

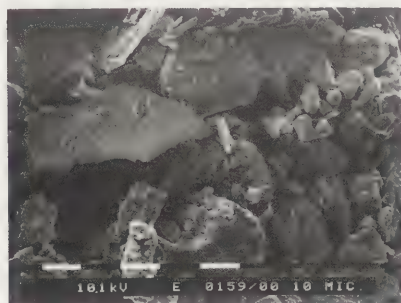


Figure 3. SEM photomicrograph showing the weathering of a feldspar grain (bottom center) and of a mica flake. Note the poor intergranular cohesion.

Description of the rock

The rock that forms this hill is a highly weathered, biotitic granitoid. It is composed of quartz, potash feldspar, plagioclases, and biotite. It can include apatite and zircon, while clay minerals, chlorite, muscovite and iron oxides are alteration products. The high degree of weathering of this rock can be seen in Figure 3.

The stone, though apparently solid, shows a high degree of microfissuration which favours a rapid weathering rate. The edges of the rock, such as the protruding end of the overhang or the sides separated by the diaclasses, are the most deteriorated areas. The continued exposure to wind and rain obviously accelerates this phenomenon. Freeze-thaw cycling can also be an important contributing factor, given the presence of foliated minerals and clays (4).

Experiment

To determine the water migration processes in this shelter, a simulated rain condition was created. The top of the overhang was partially covered with absorbent rags, protected in turn by a plastic sheet to avoid water evaporation. The surface covered was of approximately half a square meter. Two liters of

water were used during the whole experiment: half a liter to wet the absorbent material, and the rest slowly added at a rate of approximately one to two drops every two seconds. This procedure lasted some 12 hours. The cover was left on to dry and until all the measurements were taken. The "rain" event was started at 9 PM in the evening and lasted till 9 AM the following day. This was done to avoid undue evaporation by daytime exposure to the sun. The event was calculated to be equivalent to approximately 40 mm of "rain."

By means of a protimeter, the moisture content in the wall was followed from the moment the "rain" started at 9 PM. Measurements were taken in areas exposed to the "artificial rain" (C and D) and in equivalent control areas (A and B) of the shelter during the following 48 hours. The experiment was carried out twice: once in the fall during overcast days, and again in spring on clear and warm days. The data are presented in Table I.

Table I. Moisture content reading in selected areas of the shelter IW1 subjected to artificial rain (C and D) and corresponding control areas (A and B).

Season	Time hours	Temp.	% RH	Moisture contents			
				A	B	C	D
Fall (overcast)	0	10°C	88	11.0	18.5	13.0	19.5
	6	7°C	92	11.0	18.5	13.5	20.0
	12	10°C	93	13.2	22.0	14.0	23.0
	18	15°C	78	11.5*	20.0*	15.5	35.0
	24	10°C	88	13.8	22.0	15.5	30.0
	30	10°C	82	11.2	21.5	15.5	28.0
	36	12°C	87	11.0	21.0	15.5	28.0
	42	17°C	85	11.8	21.0	15.0	25.5
	48	14°C	87	11.2	20.0	14.0	23.0
Spring (clear and warm)	0	20°C	67	11.0			14.0
	6	16°C	67	13.0#			22.5
	12	18°C	70	16.0#			35.0
	18	25°C	35	12.0			23.0
	24	21°C	41	12.5			22.0
	30	19°C	62	16.0#			22.5
	36	15°C	78	14.0#			23.0
	42	21°C	35	10.0			15.6
	48	19°C	38	10.0			14.0

A = control area, back wall of shelter, rock without deposits; B = control area, vault of shelter, with clay deposit; C = area subjected to artificial rain, back wall of shelter, rock without deposits; D = area subjected to artificial rain, vault of shelter, with clay deposit; * = area received direct sunlight for a short time; # = observed dew condensation on the wall.

Note: The back wall of the shelter receives direct sunlight for nearly the whole morning.

Discussion

When the shelter is subjected to artificial rain, it can be seen that the moisture content in the inner walls increases slowly during the first six hours from the time the rain starts, and reaches a maximum after nine to twelve hours. The moisture content remains constant for some time, proportional to the length of the rain event, then the drying process begins. The rate of drying will depend on the ambient relative humidity. From previous observations, it was seen that the moisture migration followed the same pattern (3).

Moisture can also reach the walls of the shelter through two condensation phenomena: dew formation and fog-inception (5). At high relative humidities (over 75%), moisture condenses as dew on the internal walls of the shelter when there are significant temperature differences between the air and the support rock, as was observed during the spring testing at dawn and early morning. During the fall season, no condensation was observed though some fog covered the area.

On the "sound" rock without deposits, condensed moisture tends to evaporate fairly rapidly. This is not so for the areas covered with the clay layers. The presence of these deposits noticeably affects the moisture contents retained by the wall (compare values from areas C and D) and slows down the drying process. In fact, the clay layer acts as a humidity reservoir.

Conclusions and recommendations

The main factor in the deterioration of the stone has been confirmed to be the water seepage through the roof of the shelter. The walls retain moisture longer when clay deposits are present in such areas as the vault and along the water-washes. Hence, the two obvious conservation approaches would be to reduce the water seepage and to remove the clay deposits.

The removal of the clay deposit from the vault is fairly easily accomplished by light brushing. Along the waterwashes, since the deposit is more compact, brushing with some careful scraping would be needed. The problem of reducing the water seepage cannot be solved as easily. Given the shape and nature of the boulders, a thick soil cover cannot be used to reduce seepage. Other possible solutions would be the application of a water-repellent agent, or the development of an adequate cover. The authors do not favour the application of a water-repellent agent at present, since several unanswered questions still remain regarding the long-term effects of these materials. Therefore, an adequate cover needs to be developed. It must be determined through testing if a cover will protect the site as expected. For this purpose, the shelter should be only partially covered by an impermeable material in an area which would not affect the rock paintings directly. Thus, the changes in moisture content in the walls and water migration patterns could be studied. If the results proved beneficial, the whole boulder could be covered.

Given the awkward shape of the shelter, one possible solution would be to use a geo-textile to cover the surface and grow a ground-cover/creeper over it to disguise it. This would significantly change the look of the shelter, but if revegetation of the site is also considered, the overall appearance could be landscaped to integrate the covering with the existing environment.

The revegetation of the site, particularly to the left (east) of the shelter, would provide a means of diminishing the thermal variations and also serve as a wind barrier. The type of bushes and trees to be planted, and their location with regards to the shelter, has to be considered in terms of the natural vegetation of the area and the effectiveness for micro-climate improvement.

If the proposed solution of a cover is to be adopted, it should be taken into account that intensive monitoring and maintenance of the site will be required. Unless this can be provided, the protection scheme has to be adapted to fit the available management possibilities. A more realistic solution could be to consider this particular shelter as a "sacrificial site" and limit the conservation activities to those requiring minimal maintenance (6).

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Abstract

The microclimate inside the Hal Saflieni Hypogeum, Malta, was monitored both spatially and temporally over a three-year period. This included recording air temperature and humidity in the various chambers, wall temperatures and moisture content, speed and direction of air currents, carbon dioxide concentrations, and light levels. Records of the presence of water, as pools and droplets, were also kept. It was found that, either directly or indirectly, the presence of visitors, together with the associated opening and closing of doors and illumination of the site, causes the greatest disturbance to the otherwise stable underground climate. Other factors causing disturbance include changes in external atmospheric conditions and the presence of water. Readings of air temperature and relative humidity taken over the past year during which the site has been unvisited have confirmed these conclusions.

Keywords

Archaeology, Malta, monitoring, microclimate, prehistoric monument, underground temple, visitors

Visitor Impact on an Underground Prehistoric Monument—The Hal Saflieni Hypogeum, Malta

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Description and history

The Hal Saflieni Hypogeum in Malta is an underground temple dating to the period 3300–3000 B.C. It consists of a number of interconnected chambers carved in the soft Lower Globigerina limestone. It extends over an area of approximately 500 m² in three, partly superimposed levels, the lowest point reaching a depth of 10.6 m below ground level. Some of the chambers are elaborately carved in imitation of the architecture of the contemporaneous Maltese megalithic temples constructed above ground; other chambers contain decorations, including discs, spirals and hexagons painted in red ochre.

The hypogeum was discovered accidentally in 1902 when houses were being built in the overlying area (1). It was opened to the public in 1908. Although initially very few visitors were attracted to the site, numbers gradually increased, reaching a maximum of 74,000 visitors in 1987 (See fig. 1).

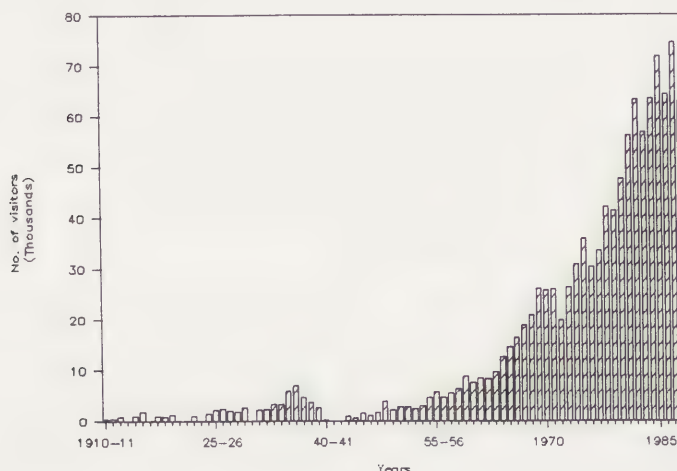


Figure 1. Annual numbers of visitors to the hypogeum from 1910 to 1988 (in thousands).

Study of the microclimate

A long-term study of the microclimate within the hypogeum was initiated in 1986 by the Museums Department in collaboration with the University of Malta (2).

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The study included the following:

- continuous recording of the temperature and humidity of the air in the various levels within the site and also in the entrance room
- regular measurement of the temperature and moisture content of the walls in several areas in all three levels
- measurement of the speed and observation of the direction of air currents during different seasons, with doors both opened and closed, and with and without visitors
- recording of light levels in the various chambers
- monitoring of the presence of water droplets and pools within the various chambers.

At the end of a three-year period of monitoring, these factors were correlated with external meteorological conditions (obtained from the local Meteorological Office) and with the numbers of visitors, in an attempt to establish a correlation between the pattern of changes and these variables, and to establish which factor had the greatest influence on the fluctuations recorded.

Changes in internal climate

As expected, it was found that both outside conditions and the presence of visitors affected conditions within the hypogeum, with visitors causing the greatest perturbations overall (3). Thus, it was observed that daily fluctuations in air temperature and humidity in the middle and lower levels of the hypogeum directly corresponded to the opening hours of the hypogeum and to the presence of visitors underground (the upper level was excluded from this study as it was already closed to the public) (4). Such changes were much less pronounced in chambers that have direct openings to the outside, which tend to mitigate these effects.

In general, when a large group of fifty or more visitors entered, the extent of the perturbation in the middle level corresponded to the size of the group, becoming more pronounced the larger the group. The mere presence of a group of visitors, together with the opening and closing of the doors to the entrance room, often gave rise to a sudden large change in internal conditions. People entering in small groups (of 10 or less persons), and the frequent but rapid opening and closing of doors gave rise to smaller registered disturbances.

In the lower level, on the other hand, the simple act of opening the doors to the entrance room was found to matter more than the actual number of visitors that entered. A narrow passage leads to the deepest chambers of the site and this limits the number of visitors who can enter this area at any one time. Hence, changes here are caused by the "piston effect," where a body of air is pushed inwards by a number of persons entering the site together. The narrowness of the passage results in a small group having the same effect as a larger group.

There were also significant differences registered in conditions within the monument at different times of the year. Thus, it was found that in winter, the internal climate in all areas was much more stable than during the other seasons. This can be explained in two ways: fewer people visited the site during this time of year, and those who entered carried in with them a body of cold air which was more compatible with the air inside the hypogeum than a similar body of air in summer. Furthermore, any registered changes were found to be much less pronounced in the lower level than in the middle level (See figs. 2, 3). This could again be due to the fact that fewer persons tended to enter the deepest chambers, or it could be because of the greater distance between the outside and the lower level, which mitigated any adverse effects, or to both reasons combined.

Of all the areas monitored, the entrance room registered the most erratic daily fluctuations. A combination of several factors may explain these fluctuations: 1) the room's location above ground, which causes it to be less "lagged" and, therefore, less buffered against outside changes; 2) the opening and closing of doors, which causes outside air to enter this area first; and 3) the fact that visitors

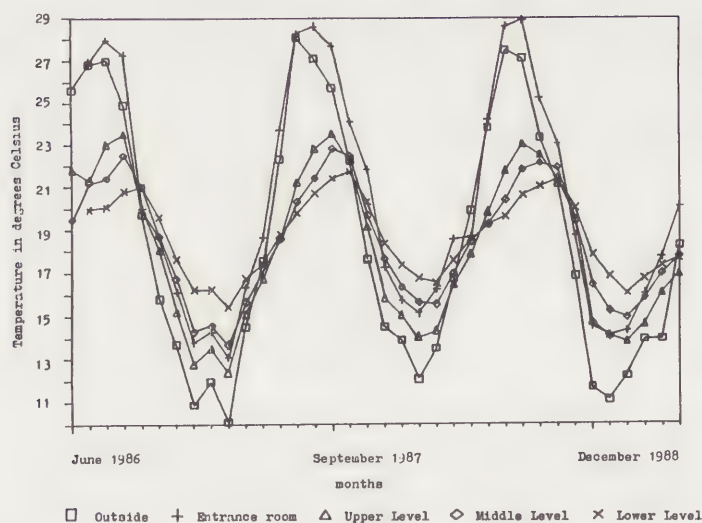


Figure 2. Mean monthly air temperature in the various levels of the hypogeum and at the exterior for the period June 1986 to May 1989.

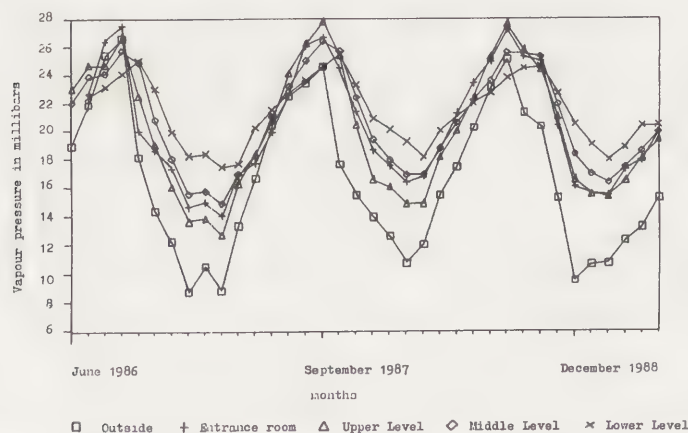


Figure 3. Mean monthly vapour pressure in the various levels of the hypogeum and at the exterior for the same period under study.

sometimes tended to congregate in this area for longer periods, although this was actively discouraged.

However, all areas monitored responded significantly to the presence of visitors because in most of the chambers the only connection with the outside is through the entrance room; there is only one other opening to the site, a ventilation shaft in the middle level. Thus, on days when the site was closed to the public, no fluctuations at all were recorded anywhere. This confirms two important points: that it is people entering and leaving the site which causes most disturbance to internal conditions, and that the microclimate of the site tends to be quite stable in the absence of such disturbances.

These conclusions have also been confirmed during the past year during which the site has been closed to visitors and the monitoring of air temperature and humidity inside the monument has continued. We can now definitely say that daily fluctuations in these parameters, especially temperature, depend directly on the presence of visitors in the underground chambers. The seasonal oscillations, especially in relative humidity, which had been attributed to variations in the external environment, have persisted, thus also validating this theory.

Air currents

Changes occurring above the ground can only be transmitted into the underground areas if detectable air currents are present. Our measurements showed that when the entrance door was closed and no visitors were present, the air movement was slow in all areas, decreasing as the distance from the entrance

increased. The lowest air speeds were registered in the lower level. With the entrance room doors closed and no visitors present, the maximum recorded air speed was of 2.0 m/s in the middle level (Autumn 1988). Slow air currents were also recorded in the entrance room when no visitors were present and the doors were closed; however, the velocity increased by about 1 m/s when the doors were opened and visitors were entering and leaving the area (5).

Carbon dioxide

Measurements taken at various points in the hypogeum showed that the lowest values of carbon dioxide were always registered in the morning before the start of visits, whereas the highest readings were always obtained at the end of the day. Besides, maxima were always found in areas which had no direct openings to the exterior, reaching a maximum of 0.4% ($\pm 0.05\%$) while the lowest values were recorded in the chamber with a direct opening to the exterior, which facilitated air exchange. Here the maximum recorded value was of 0.2% ($\pm 0.01\%$). It is interesting to note that the highest reading of carbon dioxide was recorded after a large number of visitors (263) had visited the site (6).

Light

In the past, the site, including its decorated chambers, was quite strongly illuminated, resulting in an alarming spread of algae in these areas. However, in 1986 (before the start of this study), the light intensity in the site and especially in the rooms with decorations was greatly reduced and the use of torches and flash lights by visitors was banned. The wattage of the bulbs was decreased from 60 W to 40 W in the undecorated chambers, and yellow bulbs (15 W) and yellow filters were introduced in the decorated chambers. The light fixtures were also moved away from the decorated walls and ceilings to prevent direct light from falling on them.

Measurements taken on the decorated walls in 1988 showed that the light intensity varied from 0.1 lux to 3.1 lux. However, in proximity of the light sources, values as high as 1119 lux (near a 40-W white light bulb) were recorded.

Other effects

When visitors enter the site, they carry on their clothes and bodies spores and bacteria that can increase and multiply in a suitable environment. Dust, carried into the site in the same manner, accumulates with little chance of dispersion or removal. However, the effects of spores, bacteria, and dust were not quantified.

Persons visiting a site also move about the place and more often than not touch any areas they can reach to get a "feel" of the monument. The hypogeum is a small site, with most of the side chambers being inaccessible, and so even quite small groups of visitors can find themselves in rather cramped conditions, rubbing against the walls while taller visitors actually brush their heads against the decorated ceiling. In fact, several of the painted areas show loss of pigment (7). The original floor is also being worn away by the trampling of thousands of feet (1,300,000 visitors registered from 1910 to 1988). Deliberate acts of vandalism are limited to isolated cases of graffiti in unobtrusive areas.

During the course of this study, visitors also tended to tamper with the recording instruments left in the chambers. Hence, these had to be placed in inaccessible corners and recesses, a move which must have affected the accuracy of the readings. Despite precautions, the instruments were sometimes found damaged or dismantled.

Water problems

As part of this monitoring exercise, but peripheral to the main objectives, the presence of water droplets and pools was recorded on a weekly basis. Although the presence of droplets of water within the site would seem to be a seasonal phenomenon, the appearance of pools does not always follow the same pattern. Separate studies were, therefore, undertaken with respect to this problem, confirming multiple sources for the presence of water within the site (8, 9, 10).

Remedial measures

On the basis of this long-term study a number of measures were taken to reduce as much as possible the damaging effects caused by visitors.

Following the reduction of light levels in 1986, in 1988 an automatic lighting system was introduced, with the site being illuminated for only 45 minutes out of every 90 minutes. During each 45-minute visit, only a maximum number of 60 persons were allowed to enter the site together. This timetable was in force until 1991, when the site was closed to the public. In conjunction with the construction of a new entrance to the site, which is currently under way, a computerised system of illumination is being planned that will further reduce the time during which the decorated chambers are lit (11).

The new entrance hall currently under construction also incorporates features that will create within this area a buffer zone to mitigate the effects of external changes on the rest of the monument. These features include the incorporation of insulating materials into the walls and ceilings and the installation of an air conditioning system. The number of visitors within the site will be further reduced to a maximum of 10 persons in each level, and the time visitors are allowed to spend in any one level of the monument will also be shortened. Lightweight walkways and railings are to be built to prevent attrition of the original floors and to prevent visitors, as much as possible, from touching the chamber walls.

Conclusion

The data gathered during this ongoing microclimatic study, which was initiated in 1986, has allowed a definition of the internal environmental conditions of this underground site. It has demonstrated the dependence of the measured parameters—temperature, humidity, carbon dioxide concentrations, and air currents—on external factors, in particular the presence of visitors and seasonal changes. The quantification of these variables has allowed the planning of an ambitious programme, currently underway, for the conservation of the site. This programme includes the control of air temperature and humidity within the monument. Visitor numbers will be limited to keep carbon dioxide levels low and the illumination of the chambers will be decreased to control the growth and spread of algae. If our aims are achieved and deleterious external influences on this underground site are kept to a minimum, it is hoped that the monument will do what it had been doing for thousands of years before its discovery, that is, “preserve itself.”

Acknowledgements

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Résumé

Pour le site de la grotte ornée du Cro de Granville à Rouffignac, les auteurs, après étude du contexte géologique, hydrogéologique et environnemental, définissent des aires de sensibilité et de vulnérabilité aux actions altérageuses. Cette appréciation de la vulnérabilité du site conduit à des recommandations concernant le maintien des conditions de la situation actuelle de la colline (mode d'exploitation culturale et forestière. . .). La modification de ces conditions entraînerait par voies indirectes des risques de dégradations des tracés et gravures préhistoriques de la cavité.

Mots clés

Vulnérabilité, conservation, grotte, art préhistorique, environnement, protection, géologie, altérageuse

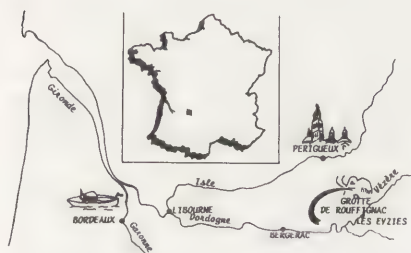


Fig. 1 : Localisation de la cavité



Fig. 2 : Représentations préhistoriques du grand plafond

Appréciation de la vulnérabilité, protection du site et de la grotte préhistorique du Cro de Granville à Rouffignac (France)

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Introduction

La grotte de Rouffignac, connue aussi sous les noms de "grotte de Miremont" ou "Cro de Granville", située sur la commune de Rouffignac (Dordogne), se trouve à environ 1 100 mètres à l'ouest du village de Fleurac et à 4 300 mètres au sud-est du bourg de Rouffignac (fig. 1). La cavité a été fréquentée par l'homme préhistorique qui a laissé de nombreux témoins pariétaux au long des galeries. Les figures ont été exécutées avec des techniques diverses: dessin au noir de manganèse (avec des crayons d'argile mêlée de bioxyde de manganèse), à l'argile rouge (rare), à la craie blanche (seul exemple au Salon rouge); tracé digital sur l'argile molle; gravure effectuée à l'aide de divers outils. L'inventaire, fait par C. Barrière (fig. 2) donne les résultats suivants: "cent cinquante mammouths, vingt-six bisons, quatorze chevaux, douze rhinocéros, douze bouquetins, six serpents, deux félins, une antilope saïga, un cervidé, un ours, une tête barbue de face, quatre figures anthropomorphes, un signe indéterminé, treize tectiformes, douze "signes", deux groupes de barres, quatre divers. Total: deux cent soixante-deux, à quoi il faut ajouter la multitude des tracés digitaux de toutes natures, dont une partie (les serpentins) pourrait peut être regroupée avec les serpents" (1). C'est cet ensemble de tracés et de gravures répartis sur la voûte et les parois des galeries qu'il convient de protéger. Le présent document aborde la protection de l'environnement externe de la cavité.

L'appréciation de la vulnérabilité d'un site karstique donné doit synthétiser toutes les études, qu'elles soient d'ordre géologique, hydrogéologique, de la qualité (s.l.) des eaux et d'environnement. Elle traduit la sensibilité de l'interface air-sol à l'égard des activités agricoles, industrielles, touristiques et la réaction du couvert végétal à l'encontre des échanges hydriques, thermiques, sans oublier les invasions parasites (chenilles, champignons, bactéries, virus, etc. . .).

Cadre morphologique, géologique, hydrogéologique

La grotte forme un "dédale de 10 km de couloirs répartis en 3 étages superposés (2); seul le niveau supérieur a été fréquenté par les artistes préhistoriques. Nous précisons que le réseau orné de la grotte de Rouffignac occupe une position "moyenne" dans le schéma synthétique du développement des réseaux karstiques en Périgord Noir. C'est un réseau sub-horizontale en éventail et de type dendritique. Il est sous-jacent à un large impluvium "convexe" développé tant sur la tranche sommitale que sur les flancs de la colline de Miremont. Celle-ci présente une morphologie adoucie agrémentée de quelques entailles ou vallons secs. C'est au pied du flanc oriental que se développe la vallée principale active au fond de laquelle coule le ruisseau pérenne de "Labinche" alimenté par une source. Cette émergence sert d'exutoire au réseau de collecte des eaux souterraines développé entre les cotes: + 170 et + 180 m (E.P.D). C'est le réseau actif actuel dont le plancher se trouve à 22 m en-dessous du plancher du réseau orné à la hauteur du "puits Dourieux" et à 39 m en-dessous de l'entrée actuelle.

Sur le plan géologique, nous retiendrons que les assises inférieures de la colline sont constituées de calcaires gréseux bioclastiques beiges qui annoncent les der-

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niers termes de l'étage Santonien. L'ossature de la colline est constituée par les assises campaniennes, lesquelles sont représentées par une puissante série carbonatée (100 m d'épaisseur environ). Cette dernière est composée de calcaires glauconieux riches en silex noirs, surmontés de dépôts crayeux encore associés aux silex, eux-mêmes surmontés de calcaires très bioclastiques et localement gréseux. L'altération a engendré une paléotopographie très marquée à la fin du Crétacé supérieur et à l'orée du Tertiaire. Les épandages continentaux issus du Massif Central se sont accumulés au Sidérolithique sous la forme de sables et d'argiles mélangés. Les phénomènes hydrogéopédogénétiques ont modifié la nature de ces dépôts au profit d'horizons indurés. L'altération superficielle se prolongeait également en profondeur et les paléodissolutions ont donné naissance à un vaste réseau karstique de type dendritique concrétisant un écoulement souterrain orienté globalement du nord-est vers le sud-ouest (2, 3).

L'adaptation morpho-structurale du réseau de drainage régional a eu une double conséquence. La première a trait au creusement du vallon de "La Binche" selon un axe nord-sud. La seconde, qui est une conséquence directe de la première, a été le recoupement de la branche orientale du paléoréseau karstique supérieur de Miremont associé à l'encaissement du drain aérien. C'est ce recoupement qui est à l'origine du dégagement partiel de l'une des trois branches court-circuitées, branche à partir de laquelle les premières "prospections" ont pu être tentées par les préhistoriques, eux-mêmes précédés vraisemblablement par les animaux, dont les ours.

Succinctement, les conditions hydrogéologiques dans l'environnement rapproché de la cavité peuvent se résumer ainsi:

- Les placages tertiaires des interfluves disséqués constituent localement un réservoir à perméabilité d'interstices de médiocre qualité. La nappe contenue dans les horizons les plus perméables est alimentée directement par les apports météoriques.
- Le ruisseau du réseau inférieur de la grotte constitue un regard direct sur la nappe permanente contenue dans ce réservoir discontinu à perméabilité de fissures, alimenté à la fois par le micro-aquifère des épandages du Tertiaire et par les précipitations. Cette nappe est drainée à l'est par le ruisseau de Labinche à la faveur d'exurgences diffuses pérennes ou temporaires.

L'activité hydrique à l'intérieur de la cavité en ce qui concerne le réseau supérieur orné, se manifeste essentiellement, dans la partie de la "Voie Sacrée" comprise entre l'entrée actuelle et l'Aven. Nous pouvons distinguer:

- Les écoulements et infiltrations du même type que ceux observés à l'Aven qui correspondent aux fins de galeries avec écoulements et épanchements retardés du Sidérolithique (Etron de la vieille), les plus proches de la surface du sol.
- Les venues d'eau diffuses à la voûte des galeries provenant de circulations d'eau dans la masse des bancs calcaires et qui doivent se caractériser par un transit plus lent que précédemment. A ces zones correspond un concrétionnement actif.

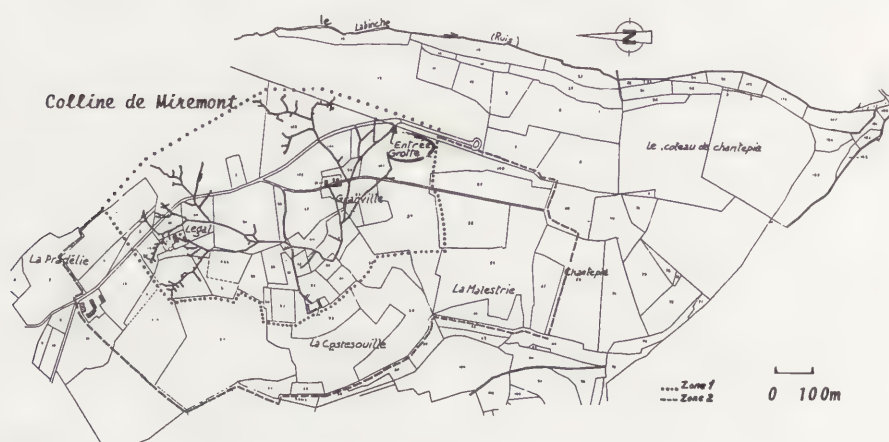


Fig. 3 : Découpage parcellaire et périmètre de protection associés à la cavité

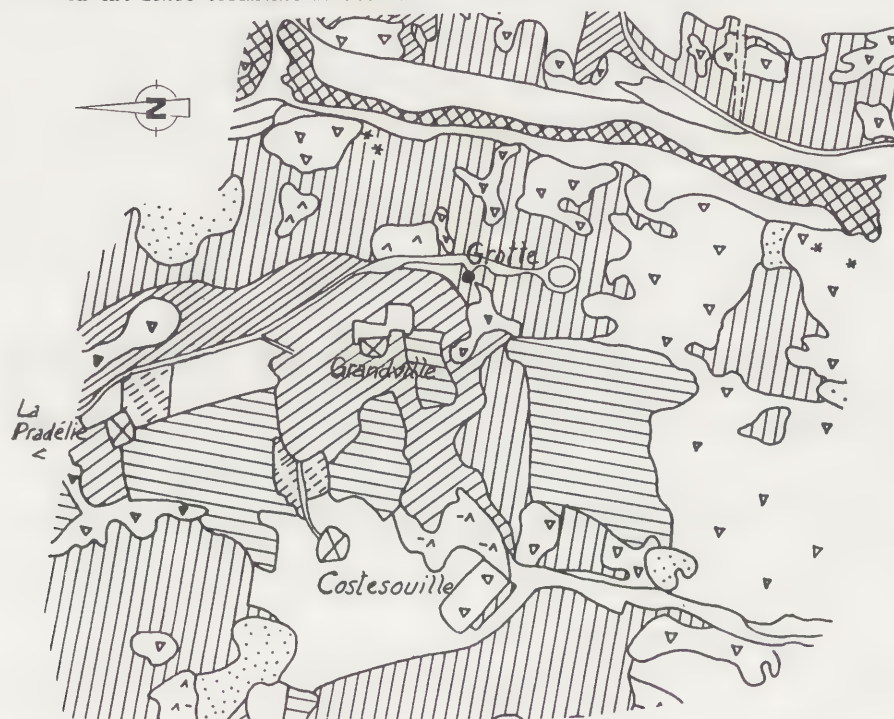
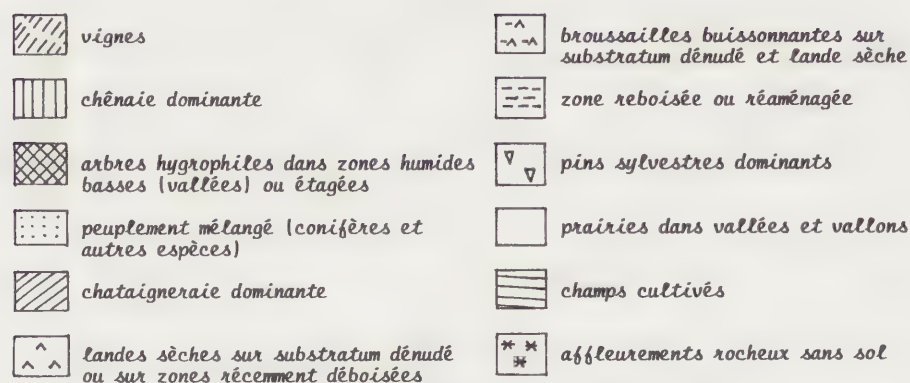


Fig. 4 : Cartographie du couvert végétal

Dans les zones actuellement ornées, aucune infiltration ni suintement n'ont été relevés. Ceci s'explique par l'épaisseur de la tranche non saturée (10 à 15 m de Sidérolithique, 45 m de calcaire) et par l'absence dans ces zones de facteurs favorables aux accumulations d'eau tels que les joints marneux, peu développés contrairement aux bancs situés plus haut (vers + 215 à 220 m N.G.F.), ou aux circulations rapides comme les conduits karstiques sub-verticaux et la fissuration des bancs calcaires.

Etat des lieux à l'extérieur

Nous avons cherché dans un premier temps à définir les limites de l'impluvium, c'est-à-dire de la surface qui recueille l'eau de pluie susceptible de s'infiltrer et de gagner plus ou moins vite le toit et/ou les parois ornées du réseau supérieur (4, 5). Ces limites ont été précisées sur la figure 3. La surface correspondante calculée par planimétrie est rappelons-le, de 0,334 Km² environ. Cette surface englobe: des exploitations agricoles et habitations, des surfaces cultivées, des surfaces en prairies, des surfaces boisées. L'importance relative des aires agraires et boisées a été calculée en même temps que nous avons dressé l'inventaire du puzzle végétal (cf. fig. 4). La mosaïque forestière est soumise aux exigences géologiques de la colline de Miremont, auxquelles s'ajoutent des conditions évolutives dans les domaines de l'hydrologie et de l'hydrogéologie.

Toute variation de l'infiltration liée à un changement saisonnier et même pluviométrique (sur deux ou trois ans) du faciès pluviométrique, sera sans conséquence immédiate sur l'évolution de la végétation arbustive dans la mesure où:

- dans le Sidérolithique, la rétention est forte au sein de la tranche non saturée et bien que la tranche saturée ne soit vraisemblablement pas exprimée
- la tranche non saturée des calcaires est très épaisse et riche en relais imperméables discontinus qui aident au piégeage momentané de l'eau souterraine
- la tranche saturée dans ces mêmes calcaires est matérialisée par des réseaux discontinus (dont la répartition spatiale est très lâche) qui restent largement au-delà de l'extension possible du réseau des racines.

Dans ce contexte, la description de la mosaïque forestière peut être résumée de la façon suivante: la chenaie couvre plus d'un tiers de la superficie étudiée. Elle constitue une forêt de versant et le sous-bois qui lui est associé, est de type "clair". La chataigneraie pour sa part représente un peu plus de 16% en surface. Elle constitue une forêt de sommet et le sous-bois qui lui est associé est de type "très ombragé". La pinède représentée par les pins sylvestres couvre en superficie presque 8% de la surface inventoriée. Elle est faite d'îlots de dimensions très variables répartis de façon hétérogène au sommet comme sur les flancs de la butte. Le boisement est à la fois naturel et organisé. Le sous-bois qui est associé à cette essence est de type "ombragé".

En définitive, nous retiendrons que le développement de la strate arbustive est bon sur l'ensemble de la colline de Miremont. Ce résultat ne préjuge pas de la capacité de chaque essence à résister avec plus ou moins de vigueur aux invasions larvaires, parasitaires, virales et cryptogamiques. Seul, le contrôle régulier de la bonne santé du couvert végétal permettra de prévenir ces attaques et d'assurer ainsi le maintien de l'équilibre hydrogéologique du sous-sol et, par voie de conséquence, l'équilibre hydrogéologique du réseau orné de Miremont.

Les exploitations agricoles et les habitations sont au nombre de quatre. Ce sont celles de "la Pradélie", de "Legal", de "Costesouille" et de "Granville" (cf. plan). Leur activité est classique pour la région et gravite essentiellement autour de la polyculture et de l'élevage de petits cheptels de bovins et des oies. Toutes ces exploitations à caractère familial sont construites à une cote supérieure à celle du réseau souterrain. Elles engendrent obligatoirement des pollutions que nous qualifierons selon les cas de domestique, liée aux activités humaines, d'animalière, liée au stockage des lisiers comme à la production des purins et autres déjections de basse-cour, d'agricole, liée au stockage, à la manipulation et aux préparations de produits chimiques utilisés soit pour l'amélioration des rendements (engrais) ou le traitement des plantes à l'encontre des maladies parasitaires (fongicides-pesticides-insecticides, etc. . .).

L'analyse de l'environnement aérien et souterrain (5) nous amène à dégager:

- des zones sensibles à la pollution
- d'autres qui le sont moins
- d'autres encore qui ne le sont pas à priori, selon la nature des terrains, l'activité au sol et la dépendance hydrogéologique des milieux aériens et souterrains.

Celles-ci sont associés à l'infiltration directe ou retardée au profit de l'aquifère discontinu drainé par le réseau orné d'une part, par le réseau inférieur qui lui est associé, d'autre part. La pollution potentielle sera une pollution domestique et agricole. La mutation agroforestière est également possible avec des retombées négatives. L'extension des aires de cultures vers l'est, l'ouest et le nord par exemple, aura des retombées tant en ce qui concerne la structure du sol (labours) qu'en ce qui concerne l'apport d'éléments fertilisants pour les plantes. L'apport d'engrais rappelons-le modifie sensiblement et à moyenne échéance, brutalement et en masse, la chimie des eaux souterraines. Cette modification peut être néfaste, dans le cas qui nous préoccupe, à la conservation des peintures préhistoriques.

Protection des sites: planification et recommandations

Les hypothèses développées au paragraphe précédent (5, 6) nous ont amenés à proposer pour le secteur d'étude, l'équivalent d'un programme de plan d'occupation des sols assorti de cartes établies sur fond topographique et fond cadastral (fig. 3). Ce plan est décrit par zone; il est assorti de prescriptions préventives dont le respect devrait assurer le maintien en l'état du support et des peintures.

Zone 1

Elle est directement superposée à la cavité ornée et s'étend également à l'amont hydraulique de celle-ci. Elle est boisée pour partie (arbres, arbustes, broussailles) et comprend des aires à vocation culturelle. Elle constitue une petite mosaïque pédologique, une aire à sol acide, argileux (rubéfié), une aire à sol basique, calcaire, blanche, une aire sans sol constituée de cailloutis calcaires affleurants.

Projet de réglementation

A l'intérieur de la zone, nous suggérons que toutes les activités autres que celles associées à la gestion de la forêt et à l'agriculture soient interdites, dans cet esprit, le manteau forestier devrait être conservé et le sous-bois entretenu. Nous suggérons que les activités agricoles associées à une irrigation intensive soient prohibées. La construction d'habitation devrait y être interdite pour limiter les risques de pollution d'origine humaine et animale. Le tracé de chemins et de tranchées sera réglementé et précédé par une étude pédologique et géologique préalable (étude d'impact).

Zone 2

Elle ceinture la zone 1 au nord, à l'ouest et au sud (cf. fig. 3). Elle comprend une fraction de terrain altimétriquement plus élevée que la précédente, au nord couverte par un sol argilo-siliceux, une surface d'altitude légèrement inférieure, au sud couverte par un sol marneux. Les deux surfaces intégrées dans cette zone participent activement à l'alimentation en eau du réseau orné. Cette surface est boisée pour partie (châtaigniers, pins et quelques broussailles) et les cultures y représentent une superficie prépondérante. L'aire ainsi délimitée est moyennement sensible à la pollution, compte tenu de la présence d'un sol, du placage sidérolithique et de l'épaississement du substratum calcaréo-marneux.

Projet de réglementation

La vocation forestière de cette zone devra être maintenue. Le déboisement sera réglementé; il pourra être autorisé sur des surfaces limitées à un ou deux hectares par an. Il sera souhaitable que les propriétaires s'engagent à reboiser dans un délai de 12 à 18 mois. La construction et/ou la restauration de ruines seront tolérées sous réserve de la mise en place d'un système d'assainissement individuel conforme à la réglementation départementale.

Zone 3

Elle constitue la fraction la plus élevée de l'impluvium qui profite à la grotte. L'altitude de la partie basse est voisine de + 260 m, celle de la partie haute culmine à + 276 m. L'horizon pédologique est rougeâtre à brun, il est à dominante argileuse. Le couvert forestier est largement dominant (90%). Les essences représentées sont les pins et les châtaigniers, les prairies et quelques champs cultivés complètent le décor. Il n'y a pas d'exploitation agricole ni de maison d'habitation. Cette surface participe à l'alimentation du réseau karstique mais la nature très peu perméable du substratum fait que les eaux circulent très lentement et donc que les temps de transfert sont longs et limitent les risques de pollution par échange et piégeage.

Projet de réglementation

La vocation agrosylvicole du site sera maintenue sans contrainte. Les règles de la constructibilité seront celles définies par le plan communal d'occupation des sols. Les activités autres, susceptibles d'altérer la qualité des eaux souterraines, seront soumises à autorisation préalable.

Conclusions

La cavité de Rouffignac est inscrite dans un cadre naturel jouant un rôle important dans sa conservation. Nous en voulons pour preuve:

- la nature géologique favorable des roches,
- la rareté des circulations d'eau souterraines,

- la faiblesse des écoulements saisonniers et leur évacuation aisée vers le réseau inférieur exempt de peintures préhistoriques en l'état actuel des investigations souterraines,
- la prédominance actuelle d'un cadre forestier par rapport aux activités agricoles,
- le maintien de ces activités agricoles dans un cadre à caractère familial que nous opposons à l'agriculture de type industriel,
- la grande extension du réseau karstique d'une part, des galeries et salles ornées d'autre part, ce qui permet le maintien d'une certaine stabilité des conditions hydroclimatiques malgré la présence des touristes,
- la sagesse des propriétaires-exploitants qui n'ont pas cherché à aller au-delà de l'objectif "préhistorique" du lieu en concentrant par exemple sur la colline des activités de plein-air les plus diverses lesquelles seraient préjudiciables au plus haut degré au maintien des meilleures conditions de protection du monument souterrain orné.

Quant à la conservation des peintures, elle est liée en plus du contexte favorable décrit précédemment:

- au maintien du régime hydrogéologique donc au maintien du canevas actuel du cadre paysager
- au maintien de la qualité physico-chimique et bactériologique des eaux souterraines, donc au maintien des conditions de vie actuelle sur la colline et à celui du rythme qualitatif et quantitatif des produits d'amendement des cultures
- à l'évolution de la couche d'altération qui recouvre les parois et le plafond ornés de la cavité.

Nous rappellerons ici que toute perturbation de l'un de ces paramètres peut modifier rapidement cet équilibre séculaire ou millénaire. Le respect des activités conseillées et suggérées sans oublier les interdictions sur la base d'une cartographie zonale fine, aura pour conséquence directe le maintien en bonne santé de ce témoin de notre passé préhistorique.

Remerciements

Il nous est agréable de remercier de leur aide Monsieur Louis Plassard, Monsieur Jean Plassard, propriétaires de la cavité et Madame Gisèle Tudela, secrétaire au L.R.M.H.

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Résumé

Bon nombre de figurations préhistoriques de la grotte du Cro de Granville (gravures, signes digitaux, tracés à l'aide de pigments) ont été surchargés de maculations (graffiti. . .) depuis 3 siècles. La lecture, la compréhension des oeuvres, leurs liens, sont gravement perturbés; la pénétration dans la roche calcaire de résidus de combustion (chandelles, lampes à acétylène. . .) est nocive pour la conservation des parois. Des interventions menées, dans le cadre d'un programme général financé par les propriétaires, en utilisant et adaptant les techniques employées pour la restauration des peintures murales des cryptes et tombes ont permis la restitution des figures masquées ou oblitérées de maculations.

Mots clés

Grotte, art rupestre, maculation, conservation, intervention

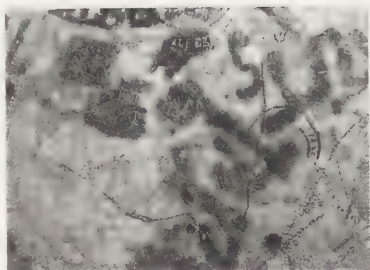


Fig. 1 : Maculation d'une figuration animale du grand plafond

Elimination de surcharges des tracés préhistoriques: quelques exemples de la grotte du Cro de Granville à Rouffignac (France)

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Introduction

La grotte du Cro de Granville à Rouffignac contient plus de 260 figures originales du paléolithique supérieur. A ces contours dessinés ou gravés s'ajoutent une multitude de tracés digitaux en signes géométriques, serpentiformes et méandres entrelacés occupant environ 500 m² de roche (1, 2). Cette ornementation en gravures aux multiples techniques, en traits noirs et en tracés digitaux est dispersée sur les parois et les plafonds de 3 Km de galeries. L'homme a fréquenté la grotte aux temps préhistoriques pour y exécuter l'art pariétal que l'on connaît. Mammouths, bisons, chevaux, bouquetins, rhinocéros, figures humaines, tectiformes, serpentiformes et méandres, constituent l'expression graphique d'un système de pensées et de croyances. La distribution des surfaces ornées et la syntaxe respectée dans ces surfaces démontrent le caractère argumenté de la démarche des auteurs de ces oeuvres. Telle est bien la différence avec l'**attitude** des curieux qui, en grand nombre, au cours des siècles précédents et surtout au 19^{ème} et 20^{ème} siècle ont eux aussi fréquenté la cavité. Succombant à la tentation d'immortaliser leur passage en ces lieux, ils ont par centaines inscrit leurs patronymes et laissé toutes sortes de maculations sur les parois de ce sanctuaire. D'importantes surfaces, dont certaines possédant des tracés originaux ont ainsi été souillées (Fig. 1). Citons l'ensemble du Grand Plafond, la Frise des Dix Mammouths, celle des Rhinocéros ou encore le Salon Rouge.

Rappelons que deux techniques ont été utilisées pour la réalisation des oeuvres: la gravure et le dessin au crayon d'oxydes de manganèse. La gravure apparaît sur tous les types de support. Dans de nombreux cas, les tracés sont exécutés au burin de silex; toutefois de grandes surfaces de roche superficiellement très corrodées sont molles. L'épaisseur de la couche décomposée varie de 1 mm à 20 mm et a souvent donné lieu à la réalisation de traits faits avec les doigts. La technique du dessin n'a été utilisée que lorsque l'artiste a jugé le support assez résistant pour abraser le crayon. Dans ce cas, le colorant est seulement accroché aux micro-aspérités de la roche. Il n'y a donc pas pénétration du pigment dans les micro-interstices. Le trait apparaît clairement en sur-épaisseur. Il va sans dire que ces faits constituent des éléments contraignants impliquant une grande prudence et un mode opératoire pouvant, dans les opérations de nettoyage de maculations, varier d'un centimètre carré à un autre.

Tant du point de vue esthétique (perte de perception des figures, mauvaise compréhension de leur ordonnancement) que de celui de la conservation (pénétration des maculations au noir de fumée dans le support. . .), l'intervention devenait nécessaire et trouvait toute sa justification à la suite de la totale réussite

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d'actions de ce type menée à Baume Latrone par I. Dangas (3, 4), Chabot et Niaux.

Après avis favorable des responsables administratifs régionaux et de la Commission Supérieure des Monuments Historiques, et compte tenu de l'ampleur des surfaces affectées par ces déprédations, de la variabilité des états de paroi et de la diversité des formes de dégradation, plusieurs phases d'intervention ont été entreprises. Trois parties bien précises ont été choisies: la frise des dix mam-mouths, la frise des rhinocéros et le grand plafond.

Etat du support des tracés préhistoriques

Frise des mam-mouths

La surface de la roche, calcaire crayeux à bancs de silex (5), a un aspect varié caractérisé par une zonation horizontale. L'examen permet de différencier plusieurs types de supports; de haut en bas:

- La partie supérieure de la frise sous un banc de silex est indurée par des concrétions très fines se présentant sous la forme d'un voile uniforme, homogène et transparent. Cependant, il existe très ponctuellement des zones de moindre dureté. Les tracés situés sur ce support durci sont actuellement en bon état, les traits sont très bien conservés.
- La partie médiane d'apparence plus claire est formée de concrétions blanches, opaques, associées à de nombreuses et fines formes excentriques. Le tracé des figurations de cette partie est estompé ou en grande partie disparu; la moitié inférieure de chaque représentation de mam-mouth est absente et seuls quelques détails (soles plantaires par exemple) font penser que les mam-mouths étaient ou pouvaient être complètement représentés.
- La partie inférieure sur une banquette est couverte de concrétions et à un aspect rouge brunâtre.

La frise des rhinocéros

La paroi revêt une forme en banquette et nous pouvons distinguer 3 parties du haut vers le bas. Dans la partie supérieure la roche est nue et présente dans la zone ornée une frange d'altération avec localement des indices de dessiccation avec formation d'écailles argilo-marneuses (5). En quelques parties, le trait bien coloré fait place, en continuité, à un tracé profond et lisse, avec peu ou pas de colorant; cela révèle un défaut de consistance du support. Dans cette zone supérieure, les traits oblitèrent les traces de dessiccation.

La partie médiane est recouverte d'une fine pellicule de calcite lisse. On ne note ni micro-concrétionnement excentrique, ni hétérogénéité de surface due à la présence de concrétion (front de concrétionnement). En quelques points seules les traces dessiccation, au moment du dépôt de la roche sont conservées sous forme de fines cloisons calcitiques.

La partie inférieure possède un important concrétionnement en "chou-fleur", de couleur rougeâtre.

Le grand plafond

C'est une surface d'érosion comme en témoignent les restes de fossiles (*Ostrea exogyra*. . .) mieux cristallisés et donc plus résistants qui sont maintenant en léger relief. Le tiers ouest de cette surface domine un puits communiquant avec l'étage inférieur; la présence de cet accident topographique naturel a joué un rôle certainement important dans le processus d'altération de la roche. Cette dernière présente ici un aspect marbré, tacheté de couleur gris verdâtre ou jaunâtre certainement due à des concentrations ponctuelles de minéraux argileux lors de la formation du sédiment. Son examen permet d'identifier divers états de paroi:

- surface claire et dure constituée d'un dépôt de cristaux de calcite lui conférant un aspect rugueux; elle correspond au haut de paroi à l'opposé du puits (bordure est). Sur ce support est tracé un groupe de trois bouquetins
- surface indurée résistant à de faibles pressions, avec une légère pulvérulence. Cet état correspond à la plus grande partie de la voûte; un très fin dépôt blanc

- pulvérulent recouvre aussi bien la roche nue, les tracés animaliers préhistoriques que les inscriptions et maculations au noir de fumée
- surface très malléable à aspect argileux
- surface à l'aspect légèrement granuleux à l'emplacement des maculations. Cet état est lié à un changement de texture sous l'effet du chauffage par la flamme des lampes à carbure aux fins de noircir la roche et ainsi d'inscrire un graffiti (dépôt de carbone dû à la mauvaise combustion de l'acétylène et à l'encrassement du bec de lampe).

Les inscriptions, maculations et désordres

On doit distinguer les dommages involontaires causés par les frottements de vêtements lors de circulations dans des passages bas ou de véritables étroitures; ainsi sous le Grand Plafond, la hauteur variait avant l'aménagement entre 0,75 et 1 m. Viennent ensuite les agressions volontaires: "toucher" des surfaces ornées, inscriptions au noir de fumée (patronyme Barry, date 2024) gravées au couteau ou avec un éclat de silex, parfois au crayon de graphite (Boutier 1902), ainsi qu'à l'argile (Brachet), tout cela combiné avec toutes sortes de traces de doigts, effleurements et maculations diverses laissant des stigmates d'autant plus marqués que le support est meuble. Notons que ces dégâts vont de paire avec le bris délibéré de concrétions dans une galerie proche de l'entrée.

Interventions

Compte tenu de la variabilité des états de surface et de la diversité des types de détériorations, l'intervention a été conduite de manière adaptée à chaque cas. Rappelons ici que les maculations de noir de fumée contiennent des résidus et des traces de matières grasses (restes imbrulés de stéarine d'une chandelle par exemple). Ces corps gras ont pu faciliter la cohésion des particules de noir de fumée. L'ammoniaque a une action émulsifiante sur les corps gras et facilite donc la dispersion des particules et leur départ par application de compresses.

A la frise des dix mammouths, malgré quelques parties très fragiles, l'état du support est satisfaisant et permet l'allègement sensible de l'inscription. Le nettoyage a commencé par le B de "Barry" à l'aide de compresses de papier absorbant imprégnées d'une solution d'eau déminéralisée et d'ammoniaque. A l'application de ces compresses a succédé un rinçage à l'eau déminéralisée par la même méthode. Selon le degré de pénétration du noir de fumée, la concentration en ammoniaque a varié de 3 à 10%. Dans les zones les plus dures un léger brossage à l'aide de pinceaux à poils tendres imbibés d'eau déminéralisée a permis de réduire les maculations. Au niveau de la partie supérieure du Y, le support noir induré a demandé une grande vigilance lors du nettoyage. A l'emplacement du recouvrement des 2 R de Barry et des tracés originaux du contour des mammouths (courbe des reins, base de l'os frontal), aucune élimination n'a été faite en raison de la fragilité du trait originel.

L'hétérogénéité du support du Grand Plafond (dureté, consistance, texture) se traduit par une plus ou moins grande faculté d'atténuation des surcharges. Quand le support est bien cristallisé, la cristallisation pouvant être antérieure et/ou postérieure aux tracés originaux et parfois même postérieure aux inscriptions, il a été possible d'alléger les surcharges à l'aide de gommes spéciales de diverses duretés. Après intervention (élimination et/ou allègement des surcharges) le bouquetin partiellement oblitéré par l'inscription Boutier 1902 est de nouveau visible. Tous les détails (Figs. 2, 3) du tracé de la figuration sont aisément identifiables. Ainsi apparaît complet "un bouquetin au dessin noir, en profil droit, . . . , une seule corne annelée en double trait, un petit trait vertical à la base et à l'arrière de la corne indique l'oreille, un oeil triangulaire vide surmonté d'un sourcil en arc. . .", tel que le décrivait Barrière (2).

Quand le support est très fragile (malléable, pulvérulent, granuleux) les variations de l'état de surface très rapides, l'allègement ou l'élimination se fait par applications répétées de "coton-tiges" imbibés d'une solution diluée d'ammoniaque ou d'eau déminéralisée suivies d'un rinçage à l'eau déminéralisée par la même méthode. La simple application de coton imbibé sur les maculations, sans frottement et sans pression, suffit à désolidariser le noir de fumée du support. L'in-



Fig. 2 : Graffiti au crayon sur une figuration de bouquetin

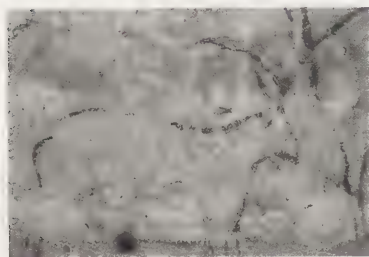


Fig. 3 : Même représentation après intervention

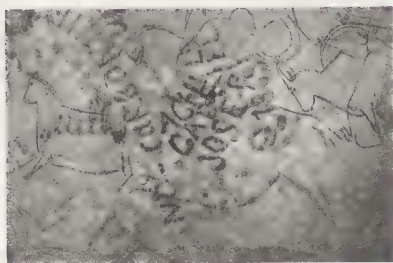


Fig. 4 : Surcharges de cet ensemble animalier

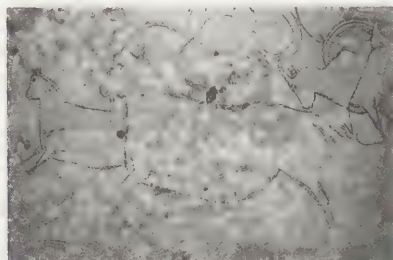


Fig. 5 : Après intervention, même ensemble

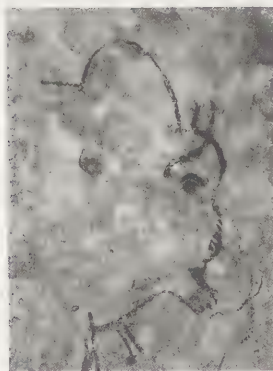


Fig. 6 : Avant-trains et tête de bison après intervention

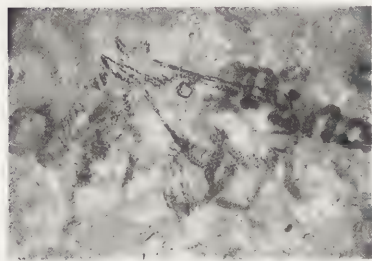


Fig. 7 : Tête de cheval avant intervention

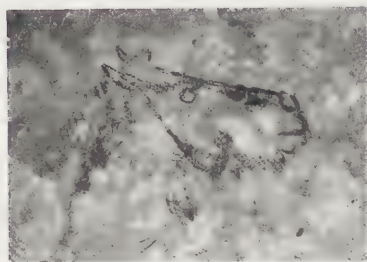


Fig. 8 : Même figure après intervention

intervention est d'autant plus délicate que localement la roche peut, à cause du chauffage par la flamme des luminaires, présenter une texture différente. Tel était le cas au niveau des inscriptions *juillet*, *achile*, *gabriel*, *joseph* et *1860* qui perturbaient profondément la lecture de deux figures de bouquetin (Figs. 4, 5). L'allègement de ces souillures a permis de restituer une bonne lisibilité à ces sujets. Un traitement identique appliqué à un avant-train de bison presque indéchiffrable auparavant, a permis non seulement de le rendre visible, mais aussi de mettre en évidence des détails qui n'avaient jusqu'alors pu être repérés et relevés (Figs. 6, 7, 8).

Les maculations à base d'argile sont plus rares. Il peut s'agir de simples frottis et lorsqu'il y a superposition avec les tracés originaux—c'est le cas des maculations recouvrant les défenses du dernier mammoth de la horde de droite de la frise des 10 mammoths—l'enlèvement s'est fait grain à grain à l'aide de scalpels et de paires de pinces fines. Lorsqu'il n'y a pas superposition, un léger grattage superficiel à l'aide d'un fin batonnet, suivi d'applications de "coton-tiges" imbibés d'eau déminéralisée permet l'élimination des taches et maculations d'argile.

Dans le cas d'inscriptions tracées en "frottis insistant" à l'argile avec oblitération d'une oeuvre, deux solutions peuvent être envisagées. La première consiste à éliminer totalement le mot ou le nom avec le risque de voir persister son négatif en plus clair sur la paroi. Il faut alors envisager de patiner ce "fantôme". La seconde méthode serait de n'enlever qu'en partie l'inscription de manière à en casser la continuité et à rendre ainsi sa perception impossible. Dans l'état actuel de notre intervention, nous n'avons pas encore fait un choix. Un traitement numérique d'image pourrait certainement nous apporter une aide en simulant le résultat recherché avec la seconde méthode.

Indépendamment des surcharges décrites, il existe des stries et divers tracés néo-gravés dans le support meuble (ces traits ont de 1 à 2 mm de profondeur). Ces détériorations apparaissent en plus clair; faut-il tenter de les patiner afin d'atténuer le contraste entre la couleur de surface de la roche et celle de ces incisions (6)? En quelques points, en raison de la faible hauteur de galerie, l'atténuation des tracés préhistoriques par le frottement du dos des visiteurs de jadis est fort importante, le marbré même de la roche est affecté; dans ce cas la dégradation est irréversible et il ne peut être envisagé aucune sorte d'action.

Conclusions

Les interventions menées en différentes parties de la grotte de Rouffignac ont montré qu'il était possible et surtout fructueux d'éliminer les éléments gênant la perception et la lecture des tracés préhistoriques de cette caverne. En outre, ce type d'action facilite le maintien en bon état des parois ornées. Comparé aux interventions menées sur d'autres biens culturels (peintures murales par exemple), ce type d'intervention est récent en France. Rappelons l'intervention de la Baume Latrone et de Niaux par Madame I. Dangas, et à l'étranger celle de Painted Rock en Californie Centrale (USA) (7), celle d'El Morro National Monument au Nouveau Mexique (USA) (8). A chaque instant, nous avons eu à l'esprit les recommandations du Ministère de la Culture: "il apparaît souhaitable que l'opération de nettoyage s'attache principalement à ce qui gêne la lisibilité des figures paléolithiques". Nous nous sommes pour cette raison toujours, dans cet esprit, cantonné à des actions ne pouvant en aucun cas mettre en danger l'oeuvre originale ni en affecter la singularité.

A ce jour, ont été conduites des actions au niveau de la frise des dix mammoths, de celle des trois rhinocéros et du grand plafond. Au total, une quinzaine de figures paléolithiques ont ainsi fait l'objet d'un "nettoyage". Les inscriptions subactuelles sont innombrables à Rouffignac. Dans leur ensemble, elles témoignent d'une histoire récente de la cavité, mais à de rares exceptions près, ne présentent pas d'intérêt individuel. Leur nombre rend donc parfaitement possible la conciliation de la mise en état du patrimoine préhistorique du site tout en sauvegardant le témoignage plus que substantiel de son passé récent.

Remerciements

Il nous est agréable de remercier ici Madame Gisèle Tudela, secrétaire au L.R.M.H.

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Résumé

Les parois ornées du Salon Noir de la grotte de Niaux présentaient des maculations, des amas vermiculaires dus au lessivage de pigments et de poussières et des dépôts d'argile oblitérant les tracés préhistoriques et constituant ainsi une menace pour leur conservation. Leur élimination a été réalisée. Parallèlement à ces interventions, est apparue la nécessité de tester des produits (conditions d'application, dilution, solvants. . .) qui pouvaient assurer le refixage des représentations préhistoriques.

Mots clés

Maculation, graffiti, intervention, paraloid B72, test de consolidation, nettoyage, art pariétal

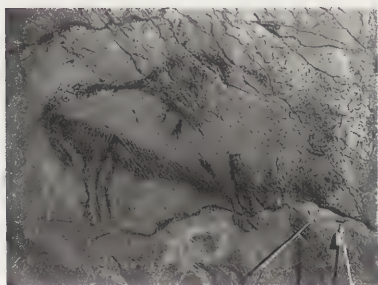


Figure 1 : Destruction de la partie antérieure du tracé d'un bison suite à des circulations d'eau

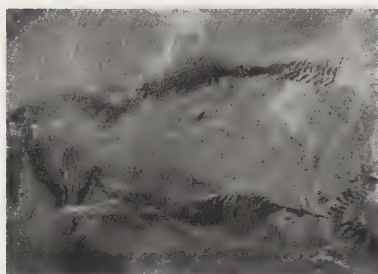


Figure 2 : Placage d'argile sur des graffiti tracés dans une figuration préhistorique

Interventions: nettoyage des parois, tests de consolidation au Salon Noir de la grotte préhistorique de Niaux (France)

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Introduction

En 1978 et 1979, les tracés préhistoriques monochromes du Salon Noir de la grotte de Niaux (Ariège) ont été victimes de ruissellements d'eau (Fig. 1) qui en déstabilisant les pigments ont provoqué la mutilation partielle et la disparition d'une dizaine de figurations animales. Afin de mieux prévoir une éventuelle évolution de la paroi ornée (reprise des circulations d'eau, écoulements par les pores et les fissures de la roche, dépôt de concrétion de calcite) mieux apprécier son état de conservation et être prêt pour des actes conservatoires, une série d'interventions fut décidée par la Commission Supérieure des Monuments Historiques. Les buts de ces interventions étaient:

- l'élimination d'accumulations d'argile présentes sur les parois
- l'élimination des graffiti au noir de fumée et de dépôts résiduels
- des essais de fixatif.

Les modalités de ces interventions ont été définies en accord avec J. Clottes, alors Directeur régional des Antiquités Préhistoriques; ont été ainsi l'objet d'interventions les 6 panneaux ornés du Salon Noir soit au total 153 représentations préhistoriques et les surfaces attenantes.

Rappelons que le Salon Noir se développe latéralement au terminus en cul de sac d'une galerie perpendiculaire à l'axe principal du système de cavités Niaux-Lombrives. C'est une grande coupole dotée de parois en surplomb où ont été tracées les figures préhistoriques (1). Les figurations pariétales y sont groupées en ensembles occupant des concavités de la paroi et séparées les unes des autres par des espaces non ornés (2, 3). La roche est un calcaire bien cristallisé, compact et la couche picturale est composée de charbon de bois et d'argile (4, 5).

Élimination des accumulations d'argile et des graffiti

Ces accumulations sont de deux origines. Les unes, sous forme de coulées couvrant d'assez grandes surfaces, se sont mises en place par ruissellement d'eau sur les parois à partir de fissures du panneau ou de cheminées emplies d'argile au-dessus du Salon Noir. Ces dépôts se sont accumulés en fonction de l'irrégularité des parois (profil et état de surfaces), sur plusieurs millimètres d'épaisseur. Les autres sont des placages d'argile mis en place par un ancien conservateur de la grotte pour masquer les graffiti (Fig. 2) sur des panneaux décorés et colmater des fissures pour tenter d'empêcher les venues d'eau. A ces deux origines correspondent deux aspects différents: les coulées argileuses naturelles sont mêlées de grains de calcite et ont une surface très humide due soit à des infiltrations par la roche, soit à des éclaboussures de gouttes d'eau; leur épaisseur peut atteindre plusieurs millimètres. Par contre, les placages sont plus minces et on discerne en quelques points les inscriptions qu'ils devaient camoufler.

Le panneau I du Salon Noir regroupant 9 figurations animales (numérotation d'après document non publié de Clottes et Vialou) illustrera le travail fait; il a été l'objet d'une cartographie détaillée de l'état des parois (cf. fig. 3) (6, 7) et l'on distinguait:

- les traces de boulettes d'argile réparties de préférence à la base du panneau: bisons 171 et 186 par exemple

* Auteur à qui la correspondance devrait être adressée.

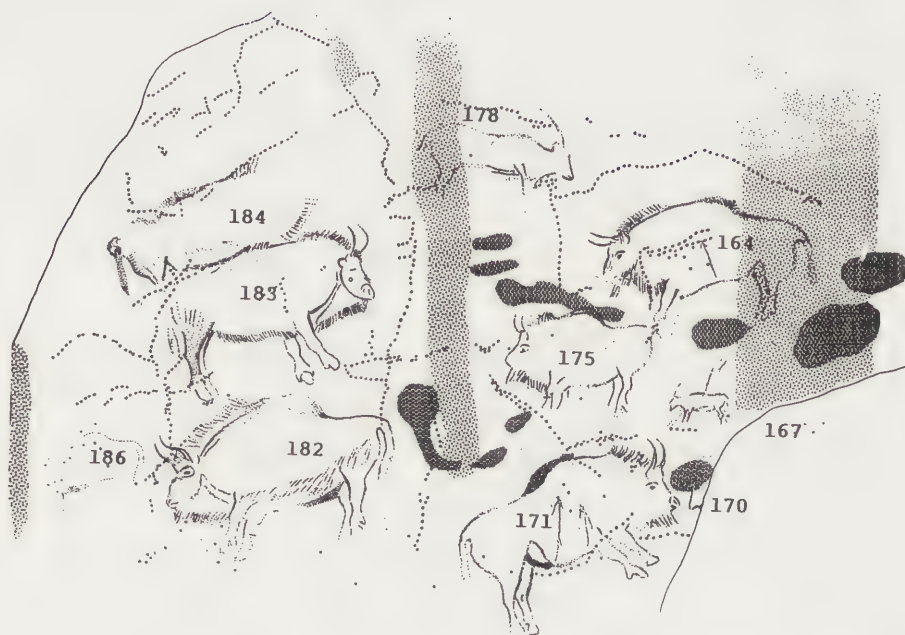


Figure 3 : Différentes accumulations de surface du panneau I du Salon Noir de Niaux (mêmes légendes que la figure 4)

- l'argile présente dans les fissures. Exemple: réseau de fissures en arrière des figurations 183 et 184
- deux "coulées" naturelles d'argile, l'une prenant en écharpe la partie postérieure du bouquetin 178 et allant jusqu'au-dessus de la croupe du bison 171, l'autre sur la partie droite du panneau recoupe le tracé du bison 164
- des placages d'argile dans le triangle des figurations 171, 184, 175, au-dessus de la tête de bison 170; entre la 178 et la 175.

Le nettoyage de l'argile s'est fait par enlèvement mécanique des dépôts superficiels à l'aide de grattoirs et spatules en alternance avec des applications de compresses de papier absorbant. Une très grande prudence a dirigé les travaux en raison de la proximité de traits originaux ou de leur existence possible sous l'argile (6). Les graffiti ont été éliminés, comme lors des premiers essais de 1983, par application de compresses de pâte de cellulose imbibées d'une solution ammoniacée. Ce dernier travail est long et délicat, car les graffiti imprègnent la roche dont la surface est rugueuse. A titre d'information, nous mentionnerons que pour les parties dépourvues de tracés préhistoriques, l'application pendant quelques minutes de pâte de cellulose reposant sur une feuille de papier japonais et imbibée de solution basique, puis des rinçages par compresses imbibées d'eau, ont permis le départ des graffiti. Pour les parties pourvues de pigments préhistoriques, l'élimination mécanique a prévalu. Quoiqu'il en soit, dans le cas de superposition de graffiti et de tracés originaux, l'opération est très délicate. Il est préférable dans ce cas d'éviter le nettoyage total. L'élimination de l'argile et des graffiti a laissé apparaître une surface couverte de cristallisations et de voiles de calcite masquant des figures.

A partir de ces plages dégagées de toute trace d'argile, il sera possible de déceler la reconstitution de ces dépôts et la présence d'éventuels ruissellements. En effet, en dépit des bourrelets mis en place en haut du panneau et de l'aménagement d'un larmier, de lentes circulations d'eau existaient au moment de l'intervention et pouvaient faciliter l'apport d'argile et l'altération des tracés peints.

Elimination des amas vermiformes

A la suite des circulations d'eau apparues en juillet 1978 ayant entraîné la destruction de figurations, nous avons remarqué la présence de dépôts résiduels sur les surfaces où le film d'eau a séjourné. Un ensemble particulièrement remarquable a été dégradé; il s'agit du panneau II où des représentations animales: cervidé 8, cheval-félin 10, cheval 11, tête de cheval 13 et avant-train de cheval 16 ont été partiellement détériorées.




Nous avons pu différencier (cf. fig. 4):

- des vermiculations noires à base de "pigments", et de produits dus à la décomposition d'un graffiti, se regroupant essentiellement le long d'une ligne passant par les bois et la ligne dorso-cervicale du cervidé, sur la ligne de poitrail, la tête et l'encolure du cheval 11, à l'encolure et à la tête du cheval 16
- des vermiculations d'argile et de poussières issues du lessivage de la paroi, dans le corps du cheval-félin 10, et une large bande discontinue entre les figures 8, 13 et 10, 11.



LEGENDE GRAPHIQUE

PIGMENTS

-  Traces ou fantômes
-  Intensité moyenne
-  Forte intensité

ACCUMULATIONS

-  Argile naturelle dans fentes
-  Argile naturelle
-  Argile en placages
-  Argile en boulettes
-  Argile en vermiculations
-  Noir en vermiculations

Figure 4 : Différentes accumulations de surface (vermiculations du panneau 2 du Salon Noir de Niaux).



Figure 5 : Représentation d'un cervidé avant dégradation

L'application de compresses de papier humidifié a permis d'enlever ces dépôts sans difficultés (figs. 5, 6). Le peu d'ancienneté (quelques années) de ces amas vermiformes a facilité le traitement de nettoyage qui s'est fait en partie par "strappo" des dépôts superficiels et en partie par absorption des derniers résidus.

Cependant, il convient d'émettre des réserves d'un point de vue déontologique, sur l'extension de ce type d'intervention. La réalisation technique du nettoyage des vermiculations peut être envisagée de deux manières et avoir diverses conséquences dans la lecture des tracés préhistoriques. L'une, l'élimination radicale du réseau de vermiculation, nécessite au préalable un refixage au niveau des traits d'origine lorsque ceux-ci sont affaiblis ou dégradés. En cas d'abrasion complète du pigment d'origine, la lecture de certains traits, ou portions de traits ne se ferait plus que par simple différence chromatique. En effet, le tracé des figurations



Figure 6 : Même figuration après lessivage par l'eau entraînant la destruction des traits des ramures et de la ligne dorsale.

a pu exercer une action inhibitrice sur les phénomènes de croissance cristalline sous les pigments; après départ des pigments le trait apparaît sous forme d'une légère "dépression" en contraste avec les microcristallisations de la paroi. L'autre, l'élimination partielle des vermiculations en "détourant" les traits d'origine aurait pour conséquences le maintien d'accumulation vermiformes sur le tracé originel et en cas de disparition totale du trait initial, la formation d'un pseudo-contour constitué uniquement de vermiculations pouvant entraîner une vision et une perception erronée et/ou arbitraire des représentations.

Entre l'élimination totale de toutes les matières "vermiculées" et le maintien de l'état actuel, en accord avec J. Clottes, nous avons choisi une solution intermédiaire répondant à un souci esthétique: l'élimination et l'allègement des vermiculations hors des tracés eux-mêmes. Ce choix a permis le départ de tout dépôt esthétiquement perturbateur.

Essais de consolidation des tracés—résultats

L'examen systématique de la paroi du Salon Noir a montré qu'en dépit des interventions menées depuis le début des dégradations, pour supprimer les venues d'eau: pose de pseudo-stalactites de polymères (travaux de Michel Garcia), aménagement du larmier existant déjà, percement de micro-forages dans la roche pour capter l'eau provenant de la masse rocheuse—matrice et fines fissures—(travaux de A. Mangin, C. Andrieux et M. Bakalowicz) (8), l'état hydrique des parois pouvait être difficile à contrôler et être même incontrôlable et qu'il fallait donc réfléchir aux possibilités offertes par des consolidations de surface par refixage. En effet, les tracés préhistoriques ont subi une altération par perte de cohésion et par désagrégation d'une couche picturale désormais constituée de particules dissociées de pigment, sur un support calcaire très humide. Dans ces conditions, il faut envisager le renforcement de la cohésion des traits peints avec un fixatif.

Dans la mesure où il sera en contact avec les tracés originaux, ce fixatif permanent doit être durable, réversible et ne provoquer aucune altération de la couche picturale. Ce fixatif devra répondre aux conditions suivantes: posséder un pouvoir adhésif suffisant, une bonne pénétration, des propriétés optiques, une résistance aux agents atmosphériques et aux attaques biologiques, une vitesse moyenne d'évaporation du solvant, une faible toxicité et ne pas favoriser l'accumulation de charges statiques. En fonction de la forte humidité des surfaces à traiter, le solvant doit avoir des caractéristiques particulières, il doit être ni aqueux, ni miscible à l'eau et posséder une basse tension superficielle. Une meilleure pénétration par une mise en solution permettra de renforcer ou de rétablir la cohésion des particules de pigments.

En fonction des critères énoncés précédemment et de résultats d'expérimentation de divers produits en laboratoire (I.C.R., ICCROM, L.R.M.H.), et in situ (dans les tombeaux étrusques de Tarquinia), deux types d'essais ont pu être réalisés à Niaux. Les uns en très petit nombre sur des plages de quelques cm² au sein même de la zone décorée et les autres dans une partie non ornée du Salon Noir à quelques mètres de l'ensemble des figurations animales sur une roche similaire pouvant être soumis à des circulations d'eau en surface ou à des venues d'eau par la porosité du calcaire, et à un micro climat souterrain (température, humidité, circulation d'air) identique à celui régnant à proximité des tracés préhistoriques.

Pour les premiers essais (plage nettoyée de placages d'argile—plage correspondant à une couche picturale très humide en cours de "lessivage" par un film d'eau—plage de pigment apparemment indemne d'altération), le refixage s'est effectué par pulvérisations appliquées en deux fois de paraloid B72 en solution à 5% dans du toluène. Le traitement est satisfaisant, près de 10 années après les plages traitées sont intactes.

Des tests systématiques ont été faits sur des plages témoins de quelques cm² reproduisant l'état actuel des figurations originales à préserver. Trois valeurs de densité de pigment noir, obtenues par frottements plus ou moins forts de bâtonnets de charbon de bois, ont été retenues; elles correspondent à des densités que nous avons fixées à 100% (noir intense et couche de pigment épaisse), à

50% (noir moins dense, le pigment est localisé sur les aspérités de la roche) à 5% (noir peu dense, le pigment laisse voir la roche). Le paraloïd B72 a été retenu comme agent de consolidation, à des concentrations de 3%, 6% et 10% dans un solvant: le toluène ou le chlorotène. L'application de la solution se faisant en une ou plusieurs fois par pulvérisation sous forme d'aérosol et/ou au pinceau. Ces différents paramètres combinés ont donné lieu à 28 plages d'essais.

L'examen des surfaces testées un an après n'a révélé aucune altération; l'hydratation de la paroi est identique, il n'y a ni coulures noires, ni vermiculations, ni concrétionnement. L'efficacité du traitement de refixage a été appréciée par applications et frottement léger de bandes de papier. Les meilleurs résultats apparaissent pour:

- les plages de densité 100%, avec un bon comportement des refixages à 3% de paraloïd en solution dans le toluène ou le chlorotène (application par aérosol et pinceau)
- les plages à 50% de densité avec un refixage à 3% de paraloïd en solution dans l'un ou l'autre solvant (2 pulvérisations par aérosol)
- les plages à 5% de densité et refixage à 3% de paraloïd en solution dans l'un ou l'autre solvant.

L'examen de ces essais, plusieurs années après application, est en cours; ils ont été soumis comme les tracés originaux préhistoriques à des phénomènes et contraintes naturels, témoins de l'évolution générale du milieu souterrain: circulation d'eau par ruissellement, dépôt de sels de calcium, échanges de vapeur d'eau entre la roche et l'atmosphère ambiante, variation d'humidité ambiante. Ces résultats feront l'objet d'un document complémentaire postérieur à la réunion de l'ICOM CC de Washington de 1993.

Conclusions

Environ 70 m² de parois ont été l'objet d'interventions; l'élimination des surcharges, maculations, dépôts facilite maintenant l'observation de l'état de la paroi et donc l'établissement de diagnostics. A ces interventions d'élimination de désordres—des effets donc de phénomènes physico-chimiques—il faut joindre les interventions-consolidations de tracés préhistoriques. A ce titre, le refixage de tracés par consolidation locale doit être pris en compte; il faut adapter les résultats d'autres disciplines aux spécificités du milieu souterrain caractérisé entre autre par le support naturel calcaire qui est une surface d'érosion, la possibilité de ruissellement et de dépôt de concrétion, la possibilité d'échange de vapeur d'eau entre la roche et le milieu aérien souterrain, la forte humidité ambiante en général. . . La connaissance du comportement de fixatifs adaptés aux nécessités du milieu souterrain devrait nous fournir à moyen terme la possibilité d'intervenir ponctuellement à titre préventif.

Remerciements

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Résumé

Dans tous les espaces souterrains décorés et/ou riches en vestiges archéologiques, les masses d'air humide en contact avec les parois sont soumises à des échanges de flux (thermiques, hydriques...) dont les incidences sont souvent très graves pour la conservation des biens culturels. Nous évoquons ici l'analyse théorique des phénomènes évapocondensatoires, des raisons de leur déclenchement, et les réactions physiques associées aux interfaces.

Mots clés

Milieus semi-enterrés, karsts, micro-climats, condensation, évaporation

Les phénomènes d'évapocondensation et la conservation des milieux souterrains archéologiques: 1. Approche théorique

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Introduction

La stabilité dans le temps des parois et du décor d'une cavité ainsi que celle des parois des objets archéologiques dépend essentiellement de leur humidité [1]. Un dessèchement trop important altère la cohésion des pigments et la cohésion des mortiers. Une condensation trop importante provoque la création d'un film d'eau permanent, continu ou non, propice au développement bactérien et algal nuisible à la sauvegarde du site, un ruissellement sur les parois pouvant entraîner des coulures et des salissures des peintures et des ornements.

La sauvegarde en milieu souterrain et des objets qu'il contient, passe donc impérativement par l'étude, puis par le contrôle de son atmosphère.

L'atmosphère souterraine (Rappels)

La vapeur d'eau

Nous n'apprenons rien à personne en écrivant qu'il existe trois états physiques de l'eau: gazeux, liquide et solide. Nous rappellerons qu'il est possible de passer d'un état à un autre par:

la fusion	}	qui absorbent de la chaleur;
la vaporisation (ou évaporation)		
la sublimation		
la solidification	}	qui libèrent de la chaleur.
la liquéfaction (ou condensation)		
la condensation solide		

La vapeur qui est en équilibre avec de l'eau liquide est dite vapeur saturante ou pression maximale de la vapeur d'eau. Nous la noterons e_w . De même nous noterons e la pression de la vapeur d'eau ou pression de vapeur sèche tant que cette pression restera inférieure à e_w . L'expérience montre que e_w ne dépend que de la température dont elle est fonction croissante. Nous la noterons $e_w(t)$. Sa variation en fonction de la température est représentée sur la figure 1.

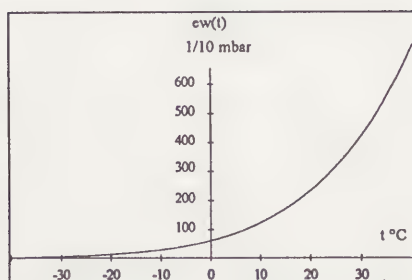


Fig. 1 : Courbe de pression maximale de la vapeur d'eau au-dessus de l'eau liquide en dixièmes de millibars.

L'air atmosphérique: mélange d'air sec et de vapeur d'eau

Aux températures habituellement rencontrées dans les milieux souterrains l'air sec et la vapeur d'eau sont considérés comme des gaz parfaits obéissant à la loi des mélanges de Dalton dont l'énoncé est le suivant: Une masse m_1 d'un gaz (1) occupant un volume V à la température T est soumise à une pression P_1 telle que: $P_1 = m_1 R_1 T V^{-1}$; une masse m_2 d'un gaz (2) occupant le même volume V à la même température T est soumise à une pression P_2 telle que: $P_2 = m_2 R_2 T V^{-1}$; en mélangeant ces deux gaz dans le volume V toujours à la température T nous pouvons constater que la pression du mélange est $P = P_1 + P_2$. P est la pression totale du mélange, P_1 et P_2 sont les pressions partielles des constituants du mélange.

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La pression atmosphérique apparaît comme la somme de la pression partielle de l'air sec et celle de la vapeur d'eau.

$$P = P_a + e.$$

- P = pression atmosphérique
- P_a = pression partielle de l'air sec = $\rho_a \cdot R_a \cdot T$
- e = pression partielle de la vapeur = $\rho_v \cdot R_v \cdot T$

On appelle air humide le mélange air sec + vapeur sèche. L'air humide est encore capable d'absorber de la vapeur d'eau. L'air saturé est le mélange air sec + vapeur d'eau saturante. L'air saturé ne peut plus absorber de vapeur d'eau. Etant donné la différence de comportement de l'air vis-à-vis de l'eau quand il est saturé ou non, il apparaît indispensable de pouvoir estimer la proximité de cette saturation. C'est ce qu'exprime l'humidité relative de l'air que nous noterons $H_r\%$. $H_r\% = 100 e/e_w(t)$, e = pression partielle de la vapeur d'eau dans l'air, $e_w(t)$ = pression maximale de la vapeur d'eau à la température de l'air (air sec: $e = 0 \Leftrightarrow H_r\% = 0\%$, air saturé: $e = e_w(t) \Leftrightarrow H_r\% = 100\%$).

Les raisons de la condensation

Saturation et condensation par refroidissement isobare

Considérons un volume élémentaire d'air humide définie par P, T_0, R_0 (masse de vapeur d'eau). Ce volume subit un refroidissement isobare. La transformation envisagée n'affecte pas la composition de ce volume c'est à dire que ce dernier conserve la même quantité de vapeur d'eau (R_0). En se refroidissant ce volume d'air voit son humidité relative augmenter. Arrive un moment où le volume est saturé. La température où le volume devient saturé est appelée température du point de rosée que nous abrègerons en T_d . Quand la température T est égale à la température du point de rosée T_d , le volume d'air est juste à la limite de la saturation. Si le refroidissement isobare de l'air continue la masse de vapeur d'eau devient supérieure à celle que peut contenir le volume; il y a alors un changement d'état de cette vapeur qui devient liquide: c'est la condensation.

Saturation et condensation par détente adiabatique

Considérons un volume d'air humide définie par P_0, T_0, R_0 . Ce volume subit une détente adiabatique c'est à dire une baisse de pression atmosphérique brutale. La transformation envisagée n'affecte pas la composition du volume c'est à dire que ce dernier conserve la même quantité de vapeur d'eau (R_0). Suivant le premier principe de la thermodynamique le volume voit sa température baisser. La masse d'eau restant la même, l'humidité relative du volume augmente. La saturation peut donc intervenir. La température du volume élémentaire d'air humide à partir de laquelle ce volume devient saturé, lors d'une détente adiabatique, est appelée température du point de condensation. Comme précédemment si la détente se poursuit il y a condensation. En général dans les milieux souterrains ce phénomène ne rentre pas en compte.

Saturation et condensation par apport de vapeur d'eau

La saturation de notre volume d'air peut aussi être provoquée par un apport de vapeur d'eau. L'origine de cette vapeur d'eau supplémentaire peut être dû à la respiration des visiteurs, à la présence de plan d'eau, à l'humidité des parois de la cavité et/ou à l'humidité des objets environnants.

Saturation par mélange avec de l'air extérieur

La saturation peut provenir du mélange isobare de particules d'air initialement non saturées, par exemple par apport d'air extérieur. Considérons un volume d'air non saturée (1) de pression P de température T_1 contenant une masse de vapeur d'eau R_1 ainsi qu'un deuxième volume d'air non saturée (2) de même pression P de température T_2 contenant une masse de vapeur d'eau R_2 et supposons un mélange d'un nombre approximativement égal de particules (1) et (2). Le mélange ainsi obtenu se trouve sensiblement dans l'état suivant: — Pression: P , — Température: $T_{air} = (T_1 + T_2)/2$ — Masse de vapeur d'eau: $R_{air} =$

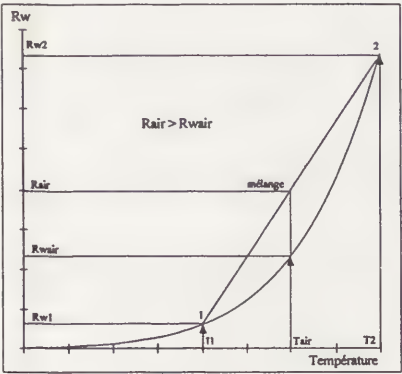


Fig. 2 : Possibilité de saturation par mélange de deux airs d'origine différentes.

$(R_1 + R_2)/2$. Etant donné la concavité de la courbe $R_w(T)$ à pression constante R_{air} peut devenir supérieure à R_{wair} . Il y a alors condensation au sein du mélange.

L'équilibre à l'interface air-parois de l'atmosphère de la cavité.

Eléments de bases

Les seuls paramètres facilement mesurables entrant en jeu dans l'équilibre air-parois sont:

- température de l'air extérieur
- humidité relative de l'air extérieur
- pression atmosphérique de l'air extérieur
- température de l'air de la cavité
- humidité relative de l'air de la cavité
- pression atmosphérique de l'air de la cavité
- température de surface des parois.

Equilibre air-parois

La masse d'air de la cavité à une température T_a en contact avec les parois de température T_p est soumise aux lois sur la condensation que nous avons énoncées ci-dessus. Ainsi lorsque la tension de vapeur de l'air est supérieure à la tension de vapeur saturante de l'air à la température de la paroi un film d'eau peut se former par condensation. L'épaisseur de ce film variera en fonction du brassage plus ou moins important de l'air en contact avec la paroi, en fonction de la nature de cette paroi et en fonction de sa porosité. Malheureusement ces facteurs sont pratiquement impossibles à prendre en compte. Inversement une tension de vapeur de l'air de la cavité beaucoup plus faible que la tension de vapeur saturante à la température de la paroi peut entraîner une évaporation de l'eau contenue sur et dans le matériau constituant cette paroi.

La température des parois de la cavité [2]

Le transfert monodimensionnel, par conduction, de l'onde thermique dans le sol est régi par l'équation:

$$\rho c(T) \frac{\delta T}{\delta t} = \frac{\delta}{\delta z} \left\{ \lambda(T) \frac{\delta T}{\delta z} \right\} \quad (1)$$

Avec: c capacité calorifique, λ conductivité thermique, ρ masse spécifique, T température, t temps, z profondeur. La variation de la température du sol est sensiblement périodique. Nous pouvons la décomposer en série de Fourier:

$$T(z=0, t) = \sum_{n=0}^{+\infty} C_n(z=0) \cos\left(\frac{2n\pi}{\omega} t - \beta_n(z=0)\right) \quad (2)$$

avec ω période du premier harmonique, C_n amplitude de la température au sol du $n^{\text{ème}}$ harmonique, β_n déphasage de la température, n nombre entier positif ou nul. Une onde sinusoïdale de courte période progresse rapidement mais est très vite amortie. Réciproquement une onde de grande période progresse lentement mais pénètre plus profondément dans le sol. C'est-à-dire que le rapport d'amplitude décroît rapidement pour les harmoniques de rang élevé (n grand). Par conséquent la température dans le sol est essentiellement commandée par l'harmonique fondamentale de période annuelle ($\omega = 365$ jours). La température du sol à la profondeur z , solution de l'équation (1) peut être approximée par:

$$T(z, t) = A_{0(z=0)} + c_{1(z=0)} e^{-z\sqrt{\pi/a\omega}} \cos\left(\frac{2\pi}{\omega} t - z\sqrt{\pi/a\omega} - \beta_{n(z=0)}\right) \quad (3)$$

fonction représentée sur la figure 3. La courbe $T(z)$ se déplace en fonction du temps en se déformant. Les maxima et minima de température suivent les courbes enveloppes:

$$T = \pm C_1 e^{-\sqrt{\pi/a\omega} z} \quad (4)$$

$\sqrt{a\omega/\pi}$ représente la constante d'espace qui caractérise l'affaiblissement expo-

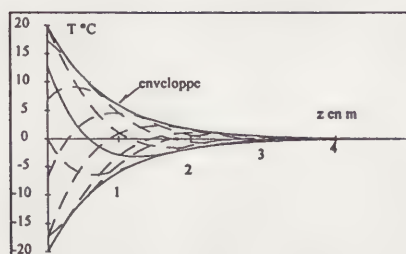


Fig. 3 : Répartition de la température dans le sol à différentes dates.

nentiel des amplitudes avec la profondeur, $2\sqrt{a\omega/\pi}$ est la vitesse de déplacement des extréma.

Applications des résultats précédents

Présentation d'un cas concret

La mise au jour de pièces et de documents archéologiques de grande valeur implique, afin d'être présentés au public, leur insertion et leur protection dans le cadre de structures appropriées. Cela conduit donc à concevoir un milieu favorable à la fois à la conservation du site et/ou de ce qu'il contient et à la visite d'un public averti. Le projet d'étude proposé a pour but de s'interroger sur les possibilités d'assurer un confort de visite tout en ne nuisant pas à la pérennité des objets présentés et du site lui-même. Concrètement, il faut envisager la possibilité de renouvellement de l'air du milieu souterrain qui est un volume clos assimilable à une cavité naturelle, par apport d'air neuf extérieur.

La température et l'humidité de l'air de la cavité

Les données météorologiques disponibles nous ont permis de construire le tableau suivant:

Tableau I. Données relatives à la climatologie. METEO FRANCE.

1946- 1990	Janvier	Février	Mars	Avril	Mai	Juin	Juillet	Août	Sept.	Oct.	Nov.	Déc.	Année
θMax	19,1	22,2	27,2	30,2	33,2	35,3	39,4	38,2	34,0	31,3	26,7	22,9	39,4
θMoy	1,9	4,0	7,5	10,9	14,9	18,2	20,6	20,0	17,1	12,2	6,4	2,7	11,4
θMin	-20,3	-20,0	-11,9	-3,6	-0,6	2,6	5,9	5,6	1,6	-4,2	-9,1	-15,1	-20,3
HrMax	95	95	95	96	98	97	94	94	98	99	97	95	96
HrMoy	84	81	75	72	75	75	72	77	82	86	86	86	79
HrMin	65	57	47	45	47	47	46	49	53	58	63	66	54

Si on accepte le principe d'un apport d'air extérieur vers l'intérieur par pompage sans autres traitements que le filtrage (dépoussiérage. . .), les valeurs du tableau I peuvent être représentatives de la température de l'air de la cavité.

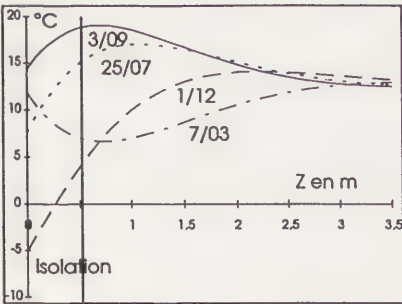


Fig. 4 : Températures théoriques des parois à différentes dates.

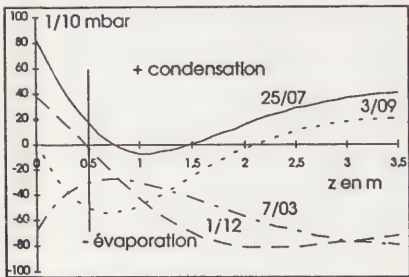


Fig. 5 : Condensation - évaporation sur les parois.

Températures des parois

Le traitement numérique des données de mesure de température enregistrées à différentes profondeurs (0,1 0,2 0,5 et 1m) permet d'évaluer la transmissivité thermique du sol au droit du site. Le report de cette valeur dans la formule (3) permet de tracer les courbes de variation de la température des parois du milieu souterrain à différentes périodes de l'année. Sur la figure 4 nous avons représenté la température des parois de la cavité à quatre dates particulières. Une bonne isolation de la voûte, puisque ce site s'y prête, nous permet de ne pas tenir compte des 50 cm superficiel.

Effet sur les parois de la cavité

Nous allons déterminer pour chaque température de la paroi la tension maxima de vapeur d'eau correspondante. Cette valeur sera comparée à la tension de vapeur de l'air atmosphérique directement en contact. Cette comparaison nous permettra de connaître l'incidence de l'air sur la paroi (condensation ou évaporation). Le résultat de ce calcul est reporté sur la figure 5. Ce site étant dépourvu de peintures pariétales, nous pouvons envisager d'accepter une légère condensation à l'interface mural. Par contre de nombreux mortiers ne supporteront pas un dessèchement. Nous voyons donc qu'il est impossible d'envoyer directement l'air extérieur dans la cavité.

Evaluation de la température acceptable

Nous allons reprendre les mêmes équations que dans le paragraphe précédent mais nous allons déterminer la température de l'air au point de rosée. Nous

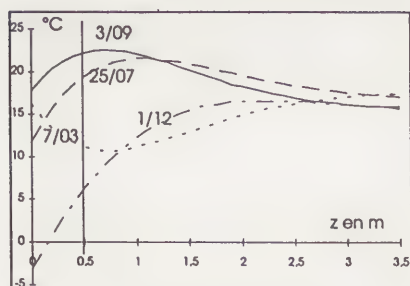


Fig. 6 : Température du point de rosée de l'air de la cavité.

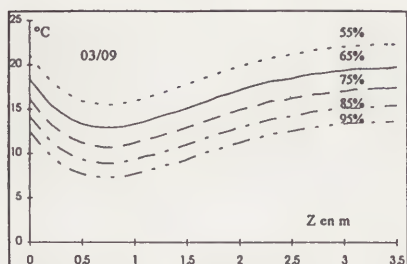


Fig. 7 : Variation du point de rosée en fonction de l'humidité relative de l'air.

obtenons les valeurs reportées sur la figure 6. Nous avons considéré que l'humidité absolue de l'air est restée constante. Ces courbes permettront à un spécialiste de la climatisation de choisir le matériel approprié. Par exemple nous voyons que le 7/03, l'air extérieur étant à 6°, nous devons le réchauffer à 15°C. Il devra être injecté de préférence sur le haut de la voûte.

Le 25/07 l'air extérieur étant à 21°C il devra être refroidi à 15°C. Dans ce cas de figure il sera préférable d'injecter l'air au ras du plancher. Une méthode plus complète devra tenir compte du changement d'humidité absolue de l'air pompé. Dans ce cas la technique à mettre en oeuvre sera plus complexe. Le refroidissement de l'air extérieur de 21°C à 15°C avec une humidité relative de 75% est le meilleur exemple où le dessèchement de l'air nous semble obligatoire. Cette variation d'humidité se traduit par des écarts importants sur la valeur du point de rosée calculé comme le montre la figure 7.

Conclusions

La mesure en continu des paramètres climatiques des ambiances souterraines naturelles ou artificielles permettra d'employer une stratégie optimale dans les problèmes de conservation sans pénaliser systématiquement les visiteurs potentiels. Cette optimisation est importante dans la recherche du coût de fonctionnement, dans celle du choix du matériel à mettre en place et dans une approche muséographique de mise en valeur du patrimoine d'âge préhistorique ou historique. Lorsque ces techniques seront parfaitement maîtrisées, une conduite automatique de la régulation pourra être envisagée. Il reste que chaque cas doit être considéré comme un cas d'espèce dont la gestion technique est réalisable selon un scénario de référence dont le canevas a été décrit ci-dessus.

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Abrégé

Enoncé avec quelques exemples, des paradoxes et des contradictions entre les notions de protection/conservation de l'art rupestre en plein air (A.R.P.A.) et les principes d'aménagement du territoire dans les parcs naturels. Critique du concept de parc naturel. Déontologie et éducation des enfants.

Mots Clés

Art rupestre en plein air, parcs naturels, aménagement conservation, contradictions

Art rupestre et aménagement du territoire: contradictions entre mise en valeur et conservation

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Problématique: énoncé des contradictions

A l'exception de l'Antarctique, l'art rupestre en plein air (A.R.P.A.) git sur les cinq continents, à toutes les latitudes, jusqu'à des altitudes extrêmes. Bien davantage que l'art des cavernes, milieux confinés à atmosphère tamponnée, l'A.R.P.A. est soumis directement aux agressions bioclimatiques naturelles et aux effets altéragegens de la présence humaine. Dans les milieux très éloignés de l'activité humaine,—milieux qui tendent à se réduire considérablement—l'A.R.P.A. ne souffre, avec une relative lenteur, que des altérations naturelles surtout liées aux variations saisonnières des climats locaux. Dans les milieux où, pour des motifs divers, l'homme manifeste sa présence, l'A.R.P.A. subit le plus souvent et de façon dramatique et accélérée, des dommages irréversibles.

Tout problème de protection et de conservation de l'A.R.P.A. inclut des intérêts ou des impératifs contradictoires dans les régions ou les sites considérés.

Une région, par exemple, étudiée récemment en Sibérie méridionale (territoire Russe), au cours d'une mission d'étude archéologique et de conservation (1), illustre parfaitement cette divergence des intérêts dans les régions d'A.R.P.A.

La construction, en 1969, d'un barrage sur le fleuve Iénisséï, à Krasnoïarsk, a créé un immense lac de retenue, de quelque 400 km de longueur, jusqu'à la ville d'Abakan (République de Khakassie) au sud. La montée progressive des eaux a immergé plusieurs centaines de pétroglyphes et de peintures rupestres gisant sur les deux rives du fleuve. Dans les années 1960, avant la mise en eau, plusieurs campagnes d'inventaire et d'archivage des oeuvres rupestres dont la chronologie s'étend de l'Age du Bronze Ancien jusqu'à l'Age du Fer, ont été menées par des équipes du Professeur Yakov Sher (Université de Kémérovo). Les documents recueillis et conservés sont les seuls témoins d'un patrimoine régional à jamais détruit.

La raison économique du développement énergétique et industriel de la région a primé, ici comme ailleurs, sur le souci de préserver, voire de respecter, le patrimoine naturel et culturel.

Dans la région de Kémérovo (Sibérie méridionale), au bord de la Rivière Tom, plusieurs stations à pétroglyphes de grand intérêt paléolithique et, souvent de belle qualité esthétique, sont connues depuis fort longtemps par les populations locales, visiteurs et chercheurs. En particulier, la station rupestre de Tomskaïa Pisanitza présente un grand intérêt pour son site naturel et pour ses pétroglyphes. L'état de délabrement des surfaces ornées est alarmant: les actions conjuguées, depuis des siècles, des érosions naturelles, surtout des desquamations liées à la schistosité du support et, depuis des décennies, des altérations anthropiques, vandalisme et travaux successifs de relevés à même la paroi (fig. 1), fournissent un exemple dramatique de ce que la nature et l'homme peuvent additionner en matière de dégradation de l'A.R.P.A.

Des universitaires et responsables locaux (Kémérovo) réalisent actuellement, selon un modèle commercial occidental, un parc naturel de loisirs, à vocation culturelle, dans le secteur de Tomskaïa Pisanitza (région du Koussbass). Par la reconstitution d'habitats traditionnels, d'espaces ethnographiques, par la réalisation d'un Musée Géologique en plein air dans la belle forêt de ce site, par la visite de la falaise à pétroglyphes au bord de la Tom, par la vente de divers objets et souvenirs, les responsables de ce nouveau parc, comme ceux de n'importe quel autre espace naturel de loisirs dans le monde, espèrent à la fois attirer le plus grand nombre possible de visiteurs et maîtriser au mieux cette zone considérée comme "protégée".

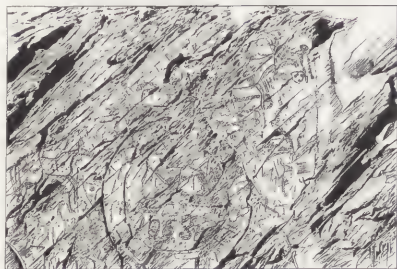


Fig. 1 Le relevé graphique micromorphologique, d'après un agrandissement photo de l'une des parois de la station de Tomskaïa Pisanitza donne un exemple typique des altérations cumulées d'origine naturelle et anthropique. La schistosité naturelle du support rocheux entraîne la microdesquamation orientée des pétroglyphes (2 élans, 1 figuration humaine, des tracés incisés...). Cette dernière est considérablement amplifiée et accélérée par les procédés de relevés des pétroglyphes en contact direct de la surface, ou bien par le vandalisme (graffiti, tentatives de dépose? ...).

Il y a dans cet exemple l'essentiel des contradictions contenues dans le concept de parc naturel (régional ou national) et dans sa mise en application sur des espaces plus ou moins vastes.

Les nécessités de la mise en valeur d'un territoire, pour son développement économique et pour améliorer les conditions de vie des populations entraînent, dans tous les cas des contraintes sur l'environnement. Proches ou non des zones industrielles et de leur cortège de nuisances et de pollutions, les zones d'A.R.P.A., plus ou moins aisément accessibles au public, subissent de façon plus ou moins apparente, lentes ou rapide, des altérations.

Dans les immenses sites rupestres d'Afrique Saharienne, loin de toutes zones urbanisées et industrialisées, l'augmentation constante, depuis une quinzaine d'années, de la pression touristique, entraîne des effets altérageux de plus en plus préoccupants sur l'environnement et sur les surfaces d'art rupestre. J'ai démontré ailleurs [9,11,12] que la seule présence du nombre de visiteurs est un facteur altérageux.

Depuis 1991, la zone des pétroglyphes du Val des Merveilles et du Val de Fontanalba, dans le Parc National du Mercantour (Alpes Françaises) est classée "rouge", mesure qui impose au visiteur plusieurs règles strictes concernant son comportement vis-à-vis des gravures rupestres. Dans le Parc National de Kakadu (Territoire du Nord, Australie), où l'art rupestre aborigène est très abondant, les circuits de visite sont précisément tracés et délimités. L'administration y est particulièrement vigilante pour la surveillance des visiteurs.

Dans les sites du Levant Espagnol, un certain nombre d'abris sous-roche décorés de peintures sont interdits d'accès par des grilles qui rappellent celles des cages de fauves d'anciens jardins zoologiques. Il n'est pas utile de multiplier les exemples pour attester que, partout dans le monde où des parcs naturels incluant des zones d'A.R.P.A. ont été créés dans le but de protéger le patrimoine, l'interdit prime largement l'autorisé. Dans certains cas, on peut se demander, au terme de cette logique de protection, si de bons films documentaires, quelques fac-similés, un diaporama, des livres, photos et cassettes, ne devraient pas remplacer la promenade dans les sites.

Les parcs naturels: effets pervers du concept et de son application

Indépendamment du souci légitime de protection de l'environnement, il y a dans le principe même de la création des parcs naturels l'idée qu'il y a deux catégories de nature: la nature où l'homme peut exercer librement son activité, quelle qu'elle soit, et la nature, ou du moins quelques espaces réduits et délimités, où la liberté d'action, y compris des activités traditionnelles est réduite, empêchée ou strictement interdite.

La vogue des parcs naturels est une résultante de la montée en puissance, dans les sociétés hyperindustrialisées, des préoccupations "écologistes" au sens large; elle manifeste aussi notre besoin fondamental de jouir de la nature dans son état... naturel. Mais cela n'implique-t-il pas qu'hors des limites des parcs, la nature continue d'être soumise au pillage? La notion d'espaces protégés induit *ipso facto* celle d'espaces où l'activité, sous toutes ses formes, est libre, avec tous les abus, tous les dangers pour l'environnement que l'on sait.

Créer un parc naturel, minuscule fragment préservé de notre planète, c'est admettre que cette planète est dangereusement menacée par des périls insurmontables, c'est reconnaître officiellement notre impuissance à empêcher ces périls, c'est, somme toute avec une certaine hypocrisie, empêcher ici, les exactions sur l'environnement qu'on ne peut éviter ailleurs.

Avec plus ou moins de discrétion dans le paysage, le statut administratif de parc naturel incluant des secteurs d'A.R.P.A. impose l'aménagement du terrain pour la protection de l'environnement et du patrimoine qu'il recèle: sentiers balisés, indications de parcours, infrastructure minimale d'hébergement, de sécurité, de sanitaire, etc. Conservatoire d'une parcelle de nature, un parc naturel est en même temps un espace destiné au public—dans certains cas le plus large possible, par souci de "rentabilité".

Il y a en réalité, dans le concept même de "parc naturel", un paradoxe fondamental. Délimiter et aménager pour la visite, des espaces de nature choisis pour leur intérêt scientifique, culturel et pour le patrimoine qu'ils recèlent, les doter d'un appareil administratif, juridique et pénal de règlements et d'interdits, sont des démarches qui vont à l'encontre de ce que, profondément, nous souhaitons trouver dans la nature lorsqu'on a la chance de pouvoir s'y promener, sortant de nos villes. Et, au bout du compte, on peut se demander si la conservation des sites, dans les parcs aménagés, peut durablement être assurée.

L'industrie du tourisme: incompatibilité du commerce, de la conservation des sites et du respect de l'A.R.P.A.

Le tourisme de masse, la démocratisation des hauts lieux de la culture universelle entraînent quasi-inéxorablement leur dégradation physique et même la perte de leur essence spirituelle. Cela est particulièrement frappant au Sahara, en Australie ou dans les Alpes, lieux privilégiés de silence, de réflexion, de sacralité, d'élévation spirituelle, où l'on peut voir des troupes de 20, 40, 60 personnes cheminer plus ou moins bruyamment, avec des comportements de groupes où la responsabilité individuelle est tellement diluée qu'elle tend à disparaître. Il est des lieux, dans la nature, qui, par leur charge symbolique, par les témoignages spirituels de la pensée religieuse des temps anciens qu'ils contiennent, doivent être préservés de toute profanation. C'est pourtant le contraire qui se produit, malheureusement à chaque saison touristique, dans les parcs naturels.

Aucune loi ne pourra jamais préserver la sacralité d'un lieu, si ce n'est une loi morale, non écrite, adoptée par chaque individu, un véritable code personnel d'éthique.

La tendance actuelle dans les sociétés industrielles et dans celles qui visent le modèle occidental, qui consiste à fondre (=confondre) culture et consommation, dans les activités dites de loisirs, représente, on le sait, une menace pour la conservation du patrimoine. Par définition, l'objet consommé est détruit ou, à tout le moins, dévalorisé. A trop consommer le patrimoine d'A.R.P.A. dans les zones protégées de parcs naturels, par un tourisme extensif, on finira par détruire, non seulement les équilibres naturellement fragiles entre l'art rupestre et son environnement, mais aussi l'esprit de cet art dans la nature, ce qui lui confère sa valeur spirituelle et son authenticité. Le problème du tourisme industriel dans les secteurs d'A.R.P.A. ne doit pas masquer d'autres problèmes, d'autres intérêts contradictoires ou même franchement opposés.

Les scientifiques ont parfois une attitude ambiguë vis-à-vis de l'A.R.P.A. En Australie, par exemple, on perçoit des différences sensibles entre les finalités du savoir des scientifiques, de la rationalité des chercheurs d'origine occidentale et les besoins de sacralité, l'"irrationalité" apparente du savoir traditionnel des Aborigènes. La divergence des conceptions entraîne des tensions, au minimum intellectuelles, entre les deux communautés quantitativement très inégales.

Ailleurs, on trouve des contradictions flagrantes, voire des conflits d'intérêts ou de pouvoirs ou encore de notoriété d'individus, entre les puissances d'argent, les marchands de loisirs, les pouvoirs publics, les aménageurs et autres promoteurs, les scientifiques, les motivations du public, etc.

Intérêts commerciaux, désirs de profits, respect des sites et des vestiges culturels, sont le plus souvent incompatibles. Comment concilier l'inconciliable?

Déontologie: conclusion

Depuis quelques années, dans la communauté internationale, spécialement chez les préhistoriens de l'art rupestre, des débats, tables rondes, colloques, congrès, introduisent de plus en plus souvent les questions de déontologie et d'éthique professionnelle chez les divers intervenants dans ce domaine. Même si, parfois, on perçoit chez certains quelque opportunisme lié à la montée de l'"écologisme" dans les mentalités et lié aussi à des désirs individuels de prééminence internationale pour le mouvement de sauvegarde de l'A.R.P.A., il faut se réjouir d'une réelle prise de conscience générale pour ce patrimoine universel gisant abondamment dans la nature.

Il reste que toute action, toute stratégie de sauvegarde, de protection de conservation sur l'A.R.P.A., ne pourront véritablement être efficaces, dans le monde entier, sans la responsabilisation des individus. Pour ce faire, la seule voie possible est celle de l'éducation, dès le plus jeune âge.

Plutôt que d'interdire et de réprimer, il s'agit de provoquer les bons réflexes de comportements et d'attitude mentale vis-à-vis de l'environnement et du patrimoine rupestre ou autre. Par l'introduction à l'école primaire d'un véritable enseignement théorique et pratique du patrimoine, la planète terre toute entière deviendra parc naturel pour les générations futures. Des enquêtes montrent que la consommation de tabac des adolescents est quasi-nulle si, pendant la première enfance, les dangers du tabagisme sont enseignés. Il en irait de même pour le respect du patrimoine dans son milieu naturel.

Un véritable progrès dans notre discipline sera accompli lorsqu'un accord international sera conclu pour introduire officiellement et obligatoirement dans les programmes scolaires publics et privés, la connaissance et le respect de la Nature et de tout ce que l'humanité y a imprimé de beau et d'utile.

Note

- (1) Mission Archéologique Française en Asie Centrale (M.A.F.A.C.) dirigée par Henri-Paul Francfort (CNRS, France) en collaboration avec le Département d'Archéologie de l'Université de Kémérov, dirigé par le Professeur Yakov Sher, du 15 juin au 14 juillet 1992. Participants français: H.-P. Francfort, D. Sacchi, F. Soleilhavoup, P. Vidal.

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Résumé

De nouvelles méthodes de collecte et de traitements automatiques du signal et de l'image sont utilisables au profit de la conservation des biens de notre héritage culturel. Nous avons développé ces méthodes au profit du suivi des paramètres climatiques et microclimatiques des grottes, des abris ornés et des sites archéologiques. Ces approches performantes permettent par exemple de suivre en temps réel la dynamique évapocondensatoire et les tendances exprimées aux interfaces. Elles permettent encore d'agir rapidement pour rééquilibrer l'ambiance interne perturbée naturellement et artificiellement.

Mots clés

Condensation, évaporation, contrôles multiparamétriques, imagerie automatique

Les phénomènes d'évapocondensation et la conservation des milieux souterrains archéologiques: 2. Etude numérique et procédures automatiques de contrôle

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Introduction

Toute prévision en matière de conservation dynamique des monuments et sites archéologiques (ou cibles), repose désormais sur la connaissance instantanée des paramètres à l'intérieur comme à l'extérieur des enceintes monumentales et archéologiques (naturelles ou construites, aériennes, semi-enterrées ou souterraines). La notion de délai dans la connaissance de l'information chiffrée est essentielle pour assurer une surveillance en temps réel de ces cibles. Les systèmes de mesure (s.l.) et d'observation utilisés jusqu'à présent nécessitaient pour justifier le coût d'investissement et l'efficacité de l'information, soit la présence sur place et en permanence d'une ou plusieurs personnes, soit des visites fréquentes des spécialistes pour relever, dépouiller, interpréter les données et agir le cas échéant. De ce fait les monuments et sites géographiquement éloignés des centres de recherches ou d'accès difficiles ne bénéficiaient que de missions condensées dans le temps d'un cycle climatique. Les chercheurs perdaient et perdent encore par cette contrainte des informations souvent essentielles liées à la fugacité temporelle d'un événement même majeur (tempête, crue, inondation, saturation en eau de l'atmosphère. . .). Pour éliminer ces inconvénients l'utilisation de centrales de mesures de plus en plus polyvalentes, autonomes en énergie et fiables est possible dès l'instant où le minitel, voire le satellite, peuvent être utilisés de façon économique comme relais dans la transmission à volonté (ou en automatique sur seuil) des informations recueillies in situ. D'autre part, certains contrôles d'événements pariétaux susceptibles d'aider à la dégradation des supports et des décors peints, gravés ou sculptés étaient longs à mettre en oeuvre et difficiles à étudier puis à interpréter. Désormais, la cartographie automatique et comparative apporte aux spécialistes une aide efficace en préalable aux interprétations phénoménologiques sans qu'il soit possible cependant de tout résoudre par cette démarche nouvelle. Nous allons illustrer par quelques exemples choisis les réalisations concrètes qui ont été faites par notre équipe en insistant bien entendu sur le fait que les mécanismes et méthodes utilisés doivent encore faire leurs preuves dans des configurations qui n'ont pas encore été envisagées à ce jour.

Principes et rappels de notions de base

Dans les ambiances climatiques où la pluie est présente quelques semaines ou plusieurs mois par an (quelle que soit la partie du monde où se trouve, la grotte, l'abri sous roche ou le site archéologique), les échanges d'eaux (vapeur, liquide) au sein des roches, des matériaux construits comme aux interfaces, sont générateurs de dégradations. Celles-ci sont lentes ou rapides, incipientes ou évidentes, simples ou complexes [1]. L'analyse théorique des phénomènes physiques est présentée dans la note précédente [2]. Dans le cas présent, nous aborderons uniquement l'étude des conséquences liées aux phénomènes évapocondensatoires et les réactions associées aux interfaces. Pour chacune des cibles évoquées ci-dessus, qu'elles soient visitées ou non, l'activité de tous les jours, comme les aménagements importants, comme encore les séquences climatiques exception-

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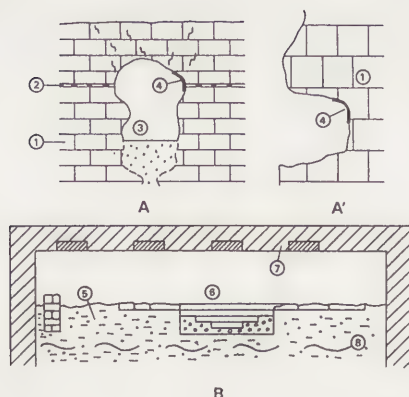


Fig. 1 : Les grottes (A), les abris (A') ornés et les sites archéologiques (B) couverts possèdent une ambiance microclimatique qui leur est propre.—1 = calcaire fissuré—2 = marne imperméable—3 = sable de remplissage—4 = peintures—5 = alluvions argilo-sableuses—6 = objet archéologique—7 = voûte bétonnée alvéolaire.

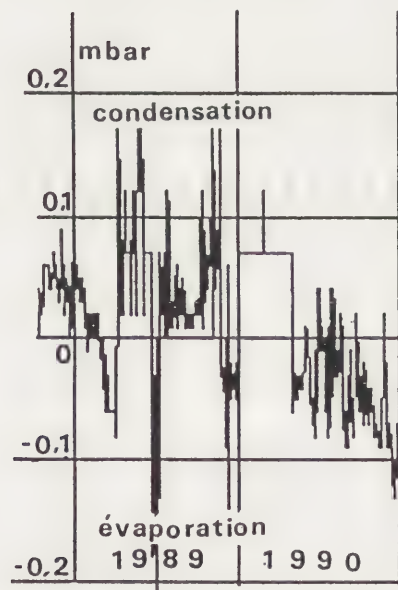


Fig. 2 : Restitution graphique des phénomènes évapocondensatoires dans le cas d'une grotte. L'analyse porte sur les années 1989 et 1990.

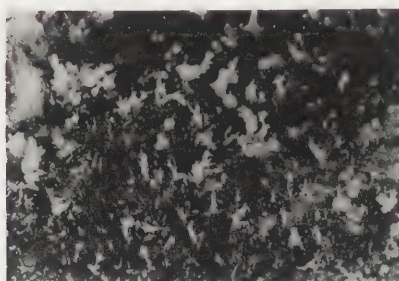


Fig. 3 : Paroi de grotte ornée riche en bourgeons calcifiés. Après évaporation, la néogenèse s'exprime par la croissance d'aiguilles fines sur ces bourgeons ($\times 5$).

nelles (sécheresse, pluviométrie intense) etc. . . sont à l'origine de processus microclimatiques, hétérogènes, révélateurs du déséquilibre plus ou moins important des tensions de vapeur de l'air et à l'interface air-matériaux. Leur déclenchement provoque plus ou moins rapidement une réaction physique ou physico-chimique superficielle ou sous-cutanée des cibles. Nous allons étudier cas par cas cette dynamique, en attribuant, dans un souci de simplification, les lettres A et A' aux grottes et abris ornés, et la lettre B aux sites archéologiques (voir Fig. 1).

Etats de déséquilibres hydriques exprimés (cas A, A', B)

La tension de vapeur des surfaces pariétales et murales de nature carbonatée ou assimilée est supérieure à la tension équilibrante de l'air environnant.

Cas A-A' : L'eau d'infiltration ou de suintement présente à l'interface (films, gouttes) rattachée chimiquement au faciès bicarbonaté calcique s'évapore (voir Fig. 2) et la calcite précipite selon des processus déjà décrits [3]. Ce concrétionnement s'exprime sous des états polymorphiques variés dont les motifs micro-morphologiques majeurs sont répertoriés dans le tableau I ci-dessous. Un exemple d'aiguilles greffées sur des bourgeons déjà formés est donné sur la figure 3. Les méthodes d'acquisition d'images et de traitement automatique permettent en phases répétitives de suivre dans le temps le phénomène de croissance cristalline (voir Figs. 4 et 5).

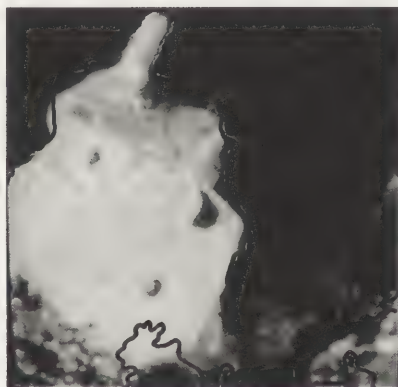


Fig. 4 : Contrôle de la croissance d'un cristal de calcite à l'aide d'un traitement d'image informatisé. La ligne continue correspond au profil enveloppe restitué 3 mois après la réalisation du premier cliché.



Fig. 5 : Cartographie de la croissance cristalline. Le trait enveloppe correspond au premier contrôle. La surface blanche est celle du cristal photographié 3 mois plus tard.

Cas B : Dans cette même ambiance évaporatrice (voir Fig. 6) l'eau d'imbibition ou l'eau capillaire contenue dans les pierres d'un mur, dans un mortier ou dans toute autre pièce archéologique poreuse et perméable, est déplacée vers l'interface ou elle s'évapore. Le phénomène est assorti ou non de précipitations chimiques et s'accompagne souvent :

- d'une décohésion des mortiers, des joints, des autres revêtements. Cette décohésion est assortie ou non d'émiettages et de mise en poussière,
- d'un blanchissement des planchers colorés constitués par exemple de briques écrasées et tassées, de débris, de tuileaux etc. . . (voir Fig. 7).

La tension de vapeur des surfaces pariétales et murales est inférieure à la tension équilibrante de l'air environnant.

Cas A-A' : La vapeur d'eau contenue dans l'ambiance abritée ou souterraine se condense sur les parois et/ou la voûte concrétionnée et ornée d'une salle, d'une galerie. Avec la persistance dans le temps de la tendance condensatoire (voir Fig. 2 déjà citée), il y a auto-alimentation en eau. Physiquement cela se traduit par la multiplication des gouttes microscopiques (voir Fig. 8) qui grandissent et fusionnent dès qu'elles se touchent. Les méthodes d'acquisition d'images et de traitement automatique permettent d'identifier les gouttes, en particulier sur un

Tableau I. Identification des néogénèses et néonécroses calciques influencées par les phénomènes évapocondensatoires exprimés dans une grotte ou un abri orné.

Phases de néoformations (polyformismes) (tendance évaporatoire exprimée)	Phases de néonécroses ou ablations par corrosions, dissolutions (tendance condensatoire exprimée)
<ul style="list-style-type: none">● précipités ponctuels, en amas, en plages: amorphes,● néogénèses simples, complexes (chaotiques, monstrueuses),● grefes d'aiguilles sur supports plans ou conchoïdaux,● bourgeonnements ponctiformes désordonnés, organisés, voiles, flocons.	<ul style="list-style-type: none">● cratérisations,● ablations (de sommets d'aiguilles et de micro-coulées),● écaillages,● boursouflures préalables, pertes de cohésion

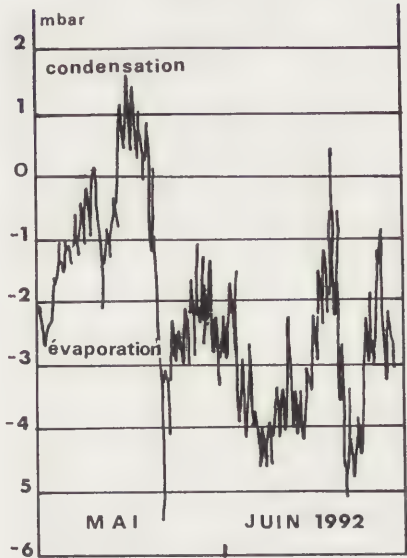


Fig. 6 : Restitution graphique des phénomènes évapocondensatoires dans le cas d'un site archéologique couvert par une dalle artificielle. L'analyse porte sur les mois de Mai et Juin 1992.

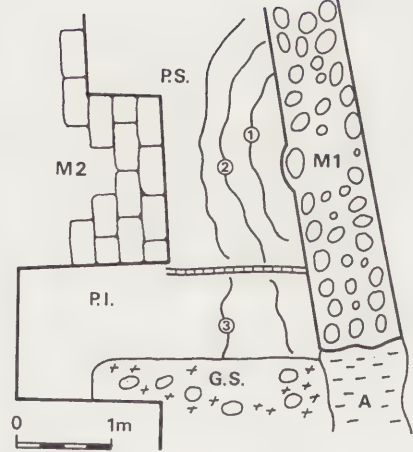


Fig. 7 : Cartographie évolutive du blanchissement (b) par évaporation interfaciale de planchers superposés faits de briques et tuileaux concassés—1: 31.03.93—2: 01.06.92—3: 22.09.92. P.S. = plancher supérieur, P.I. = plancher inférieur, M1-M2 = murs arasés, A = argile, G.S. = galets scellés.

support peint (voir Figs. 9 et 10). Les interactions de ces gouttes les unes avec les autres conduisent à des migrations selon la micromorphologie calcique. Ces migrations aident au mouillage pariétal, au ruissellement et dans les cas limites au lessivage et à l'étalement des pigments organiques (charbons de bois) ou minéraux. Leur contrôle préventif est essentiel pour la conservation de l'art pariétal. Rappelons que dans une situation de mouillage pariétal homogène sans ruissellement l'effet "loupe" du film d'eau aide à une meilleure perception visuelle des superpositions peintes (Fig. 8 déjà citée).

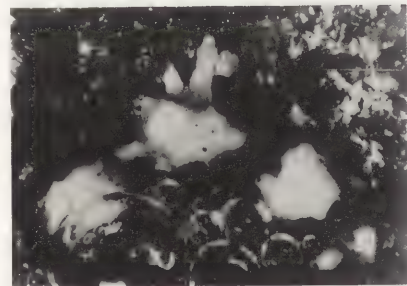


Fig. 8 : Paroi de grotte ornée (détail). En phase de condensation exprimée, les gouttes de taille variable s'accumulent dans les espaces limités par de nombreux bourgeons (x50). Les pigments de manganèse semblent jouer le rôle de catalyseur pour la condensation.



Fig. 9 : Extrait d'une surface peinte avec du manganèse sur une paroi calcaire recouverte de calcite en bourgeons.



Fig. 10 : Identification pariétale des gouttes de condensation après traitement informatisé de l'image. La surface traitée correspond au quart avant supérieur de la figure 9.

Cas B : Exemple d'un site archéologique urbain à constructions murales et en planchers imbriqués, édifié sur des alluvions fines (limons), moyennes (sables argileux) et grossières (graviers), très très proche du niveau moyen de la nappe alluviale. Ce site a été conforté par la construction, en ceinture, de parois moulées; il a été recouvert en outre par une dalle bétonnée composite. Le chantier qui lui est associé reste actif sous la forme de la poursuite de fouilles localisées sous éclairage, 8 heures par jour. L'enregistrement en continu des températures du sol, du sous-sol, de l'air, des parois ainsi que celui de l'hygrométrie de l'air permet de calculer en temps réel le déséquilibre des tensions de vapeur et d'agir, si nécessaire, par des extractions d'air provoquées par pompage. Dans le cas du développement d'une phase condensatoire (voir Fig. 6 déjà citée), il est possible de contrôler la dynamique hydrique pariétale (ici en voûte) après le traitement automatique des images. Les cartes répétitives révèlent le mode de croissance



Fig. 11 a-b: Cartographie automatique du suivi de l'évolution pariétale des gouttes de condensation à la voûte horizontale du site archéologique (a) = 25.03.92, (b) = 28.03.92.

des gouttes (voir Fig. 11 a et b). Celles-ci s'accrochent sur les hétérogénéités de la voûte horizontale et abaissent la barrière d'énergie nécessaire à la formation d'un interface continu liquide-vapeur (film automouillant). Les gouttes de petites à espacées, grossissent aux dépens de la vapeur puis fusionnent entre elles. Lorsqu'elles atteignent leur taille limite, elles tombent et arrosent le sol, les constructions et objets archéologiques. La répétition acyclique des phénomènes de désaturation des milieux par évaporation suivi de la réimbibition par chute d'eau de condensation en voûte tend à la déstabilisation des matériaux de faible cohésion.

Conclusions

Dans les milieux naturels souterrains, abrités et couverts, les altérages d'ambiance climatiques, ne se manifestent pas de façon régulière mais plutôt selon des enchaînements anarchiques dans le temps et en intensité. Le suivi de ces fonctions par enregistrements transmis directement au centre de contrôle permet une surveillance constante, une analyse et une intervention rapides si nécessaire; il en est de même pour le suivi de la phénoménologie pariétale restituée par cartographie répétitive. Le télécontrôle et la téléobservation n'en sont qu'à leurs débuts; cependant les acquis technologiques et scientifiques permettent d'envisager raisonnablement des progrès décisifs dans les années à venir. Ces progrès conduiront à une conception méthodologique globale. Celle-ci sera une aide majeure à la compréhension et à la surveillance du patrimoine monumental et archéologique quelle qu'en soit leur situation géographique et climatique.

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Working Group 25

Control of Biodeterioration

Contrôle de la biodétérioration



Abstract

The mortality of all commonly found museum pests in a nitrogen atmosphere (less than 0.1% oxygen) was evaluated at 25°C and 55% relative humidity. Fumigation methods which involve enclosing the object in heat sealable plastic bag, and the use of nitrogen and/or an oxygen scavenger are discussed. The feasibility of using nitrogen for fumigation in commercial fumigation bubbles as well as conventional fumigation chambers is also evaluated.

Key words

Fumigation, anoxia, pests, nitrogen, modified atmospheres, Ageless®

Nitrogen Fumigation: A Viable Alternative

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Introduction

In museums, fumigation with traditional chemicals is unsafe. Such chemical fumigation can cause harm to the fumigators, destroy the environment, and possibly damage rare antiquities and artifacts (1, 2).

Surveys of natural history museums and art museums indicate that beetles belonging to the families Anobiidae and Dermestidae and moths belonging to the family Tineidae are major pests (3). A list of commonly damaged materials in museums and their associated pests has been provided by Srock (4). Other groups such as termites and silverfish can be especially important in southeast Asia (5).

Theory of modified atmospheres

Considerable research has been conducted with the use of modified atmospheres to manage insect pests in stored grains and food. In most studies the lowest range of O₂ concentrations tested were 0.6–0.9%.

Marzke *et al.* found that three-day exposures at 0.5% O₂ at 26.7°C provided 100% kill of adults and larvae of *Trogoderma glabrum* (Herbst) (6). Adults were more susceptible than larvae. Navarro found that exposure time was the critical factor for certain species, such as the rice weevil *Sitophilus oryzae* (L.) (7).

Jay *et al.* found that as the relative humidity decreased, the mortality of three insects common to stored products increased when exposed to low O₂ atmospheres (0.8–0.97%) (8). Jay and Cuff found that mortality and water loss with *T. castaneum* was low at 97% N₂ and 3% O₂, but high at 99% N₂ and 1% O₂, suggesting that water loss is the major cause of death at high N₂ atmospheres (9). Gilberg found that seven day exposures at 30°C and 65–70% RH to 0.4% O₂ in nitrogen killed webbing clothes moths, cigarette beetles, drugstore beetles, carpet beetles and powderpost beetles (10). Valentin showed that exposures to 1.0% O₂ atmospheres for 20 days killed deathwatch and powderpost beetles (11). Valentin and Preusser found that 30-hour exposures to 0.5% O₂ and 99.5% N₂ atmospheres completely killed fruit flies (12). Exposure time decreased as the temperature at which the exposures were conducted increased. Rust *et al.* evaluated the mortality of all life stages of webbing clothes moths, furniture carpet beetles, firebrats, cabinet beetles, larder beetles, cigarette beetles, confused flour beetles, cockroaches, powderpost beetles, and western drywood termites at 55% RH and 25.5°C in a nitrogen atmosphere (less than 0.1% oxygen). The time required for 100% kill varied from three hours for the adult firebrats to 192 hours for the eggs of the cigarette beetle (13).

Ageless®

Ageless® is an oxygen scavenger patented and produced by the Mitsubishi Gas Chemical Company. Stated by Mitsubishi to be a mixture of finely divided moist iron (ferrous) oxide and potassium chloride, it is available in several different compositions and Ageless-Z® is the type suitable for application in conservation. Ageless-Z® is designated as Z-100, Z-1000, etc., to indicate the milliliters of oxygen with which a single packet will react.

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An important use of a material such as Ageless® is to extend the life of a low-oxygen sealed case or bag filled with an inert gas by reacting with any oxygen that leaks into it. To maintain a low concentration of oxygen in a sealed case or bag, any oxygen leaking into the case must immediately react with the Ageless®, i.e., the leak rate cannot be greater than the rate of reaction of Ageless® with oxygen. Based on the leak rate in ppm of oxygen per day, L , and the Ageless capacity, C , which is defined as the amount of Ageless® in liters divided by the volume of the case or bag in liters, one can obtain the desired equilibrium concentration using expression $[O_2] = L/12.7 C$.

For example, 12 packets of Ageless® Z-2000 can maintain an equilibrium oxygen concentration of less than 0.1% in a 1000-l case leaking 300ppm (.03%) per day (14).

Methods and discussion

Although the basic procedure is a simple one of displacing almost all oxygen from a bag, there are three variations in protocol for inducing anoxia of insects in a museum piece using a large plastic bag.

The first variation is called the dynamic system. An inert gas is used to flush all air out of the bag by an initial rapid flow rate and then, when a level of around 0.1% oxygen is reached, the flow is reduced to that required to maintain the low-oxygen atmosphere for the period of fumigation (15).

The second variation is called the dynamic-static system. The bag is purged with an inert gas as before, after a 0.1% oxygen level is achieved by a rapid flow of inert gas through the bag, an adequate amount of oxygen scavenger is quickly inserted, the gas flow stopped and the bag sealed for the required time period (16).

The static system is the third variation. This technique is ideal for the fumigation of small objects (less than 100-l). No purging is necessary. A calculated number of Ageless® packets based on the volume of oxygen to be absorbed as well as the equilibrium oxygen concentration to be maintained, is to be inserted to reduce and maintain the oxygen concentration at 0.1% for the fumigation period.

The main features of each procedure, including bag construction, relative humidity control, and experimental protocol are detailed below.

Bag construction

Plastic films vary in their permeability to oxygen. Principal criteria for selection are low oxygen permeability, availability in convenient sizes and heat sealability. For our anoxia experiments we have used Aclar (poly(chlorofluoroethylene)) extensively. Cryovac (Poly(vinylidene chloride)), which has a lower oxygen permeability, is another material which has been widely used by other conservators. (It was not available in adequate width as well as in smaller quantities for our application.)

The bags were fabricated by sealing large sheets of plastic with a heated hand sealer to yield a form conforming to the shape of the object. Precise circular holes were cut for the Swagelok fittings with a punch. Figure 1 shows the object enclosed in a heat sealed bag with relative humidity control and other instrumentation.

Relative humidity control

To avoid possible hygrometric shock to a museum object undergoing anoxic treatment in the plastic bag, the dry nitrogen from the cylinder was humidified to the object's optimal RH before being allowed to flow into the bag. The RH apparatus is shown in the background of Figure 1, and a schematic is in Figure 2. The system involved splitting the gas flow from the nitrogen cylinder into two valve-controlled lines via a tee. One line bubbled the nitrogen through water in a stout polypropylene bottle; exiting the bottle, the moist nitrogen joined the other (dry) flow of nitrogen in a mixing chamber, which flowed to a third bottle containing an RH sensor. By controlling the needle valves on the

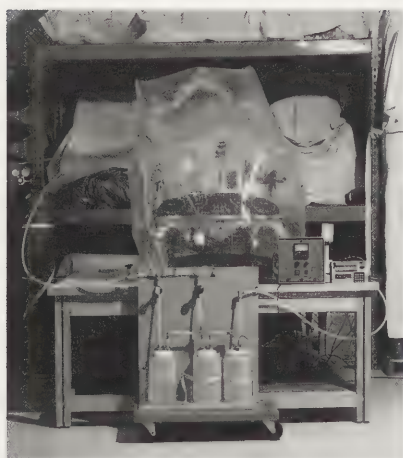


Figure 1. Anoxia setup of Italian armchair.

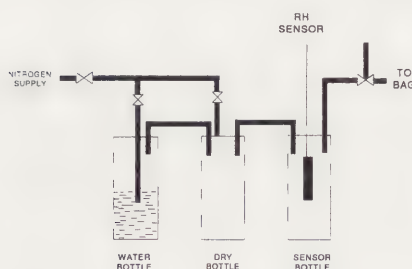


Figure 2. Schematic of humidification system for nitrogen flow.

two lines, the ratio of wet to dry nitrogen was varied to achieve the desired RH in the combined nitrogen stream which subsequently went to the plastic bag containing the object.

To minimize the influx of oxygen, all fittings from the nitrogen cylinder to the entrance of the bag used $\frac{1}{2}$ inch brass O-ring sealed Swagelok fittings. Poly(propylene) tubing ($\frac{1}{2}$ inch) led to O-ring sealed fittings in holes that had been precisely drilled in the humidification bottles. A tee fitting with an on/off valve was attached between the sensor bottle and the bag. This allowed any nitrogen whose RH was being varied prior to achieving a final RH value to be exhausted to the room atmosphere.

Fumigation procedure

The bag around the object was initially purged with a high flow rate of nitrogen conditioned at 55% RH; the oxygen concentration, relative humidity, and temperature in the bag were monitored. During the flushing at this high flow rate, the relative humidity inside the bag should be constantly monitored. A six to eight inch gap was left open on one corner of the bag opposite the nitrogen inlet to allow efficient flushing, without pressurizing the bag. This opening was heat sealed once the desired stable oxygen concentration was achieved.

In the dynamic system protocol (i), after reaching an oxygen concentration of 0.1%, the nitrogen supply was decreased to a low flow rate to maintain the desired oxygen level. In the dynamic/static system protocol (ii), the nitrogen flow was turned off and the inlet and outlet valves to the bag closed. This setup was maintained for four days to determine the leak rate of the bag. Figure 3 shows a typical example of the leak rate of a 500-L Aclar bag. After this period, the bag was cut open on one edge and with the nitrogen flowing at a high rate, Ageless[®] oxygen scavenger packets were spread out on a tray, the tray inserted and the open side heat sealed, and the nitrogen flow was turned off. The number of Ageless[®] packets was based on the amount of oxygen leaking into the bag, the oxygen absorbing capacity of each Ageless[®] packet, and the desired equilibrium oxygen concentration to be maintained. The equilibrium oxygen concentration inside a 500-L bag with 10 packets of Ageless[®] Z-2000 having a leak rate of 500 ppm is shown in Figure 4.

Moving the oxygen sensor vertically within the chamber provided an indication of the stratification of the oxygen concentration in the bag. During the fumigation of a 1500-l bag enclosing an Italian arm chair (See Figure 1) at a constant slow flow rate, as well as during the fumigation of a 2000-l bag enclosing an Italian table maintained at less than 0.1% using Ageless[®], there was 0.01% difference in oxygen concentration when the sensor was moved from a height of 80 cm to 30 cm from the floor, hence there was no significant oxygen stratification inside the bag.

The procedure for fumigating a small object (volume less than 100L) would be identical to the above, except that the third protocol of inserting a calculated number of Ageless[®] packets inserted into the plastic bag enclosing the object without any initial purging can be used. The note of caution is to make sure the Ageless[®] packets do not touch the object since the reaction of Ageless[®] with oxygen is exothermic and the surface of the ageless packets get very hot in contact with high oxygen atmospheres.

Standard bubbles and fumigation chambers

Inquiries from a number of conservators in the United States who have large scale fumigation problems suggested that any procedure involving making a large number of bags will be troublesome, hence we tested the feasibility of using a reusable standard bubble, as well as conversion of existing fumigation chambers to use nitrogen. The bubble manufactured by Rentokil corporation when fully inflated measures 11'6" \times 11'6" \times 8'3", and is widely used by conservators who have large scale fumigation problems (17). The bubble, designed for toxic gas fumigation, consists of a top cover attached via a zipper to a base sheet. In experiments at the Fine Arts Museum in Houston, we could

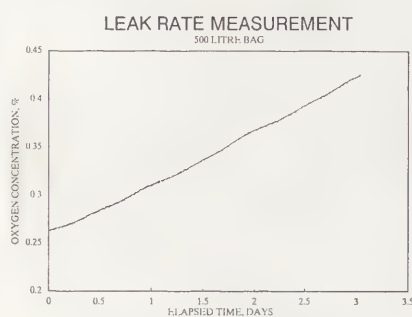


Figure 3. Leak rate measurement: oxygen concentration vs. elapsed time for 500-l Aclar bag.

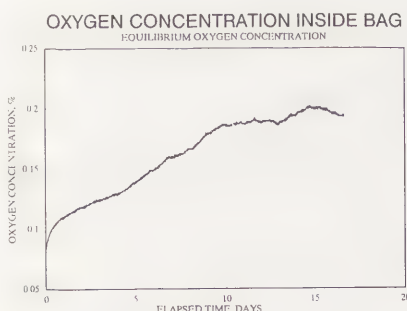


Figure 4. Equilibrium oxygen concentration maintained by a 500-l bag with 10 packets of Ageless Z-2000 and having a leak rate of 500 ppm per day.

reduce the oxygen concentration to less than 0.1% by repeated purging with nitrogen gas and evacuating the bubble, we evaluated the leak rate to be 0.08% (18). By using a similar technique of purging and evacuating, we are presently evaluating the feasibility of converting existing fumigation chambers designed for toxic gases to use nitrogen.

Future work

The study by Rust *et al.* proved the efficacy of using nitrogen with less than 0.1% oxygen to kill all life stages of the ten species studied. Although it is possible to maintain a 0.1% oxygen concentration, this may not be easily achievable in all situations as well as for all the methods described above. To increase the practical application of low oxygen fumigation, we are studying insect mortality at oxygen concentrations of 0.3, 0.6, and 1.0%. This will establish the relationship between oxygen concentration and mortality. Since the earlier study was at 55% RH we will also evaluate the mortality at 33% RH and at 75% RH to determine the effect of relative humidity on mortality. We are also currently working on the conversion of existing fumigation chambers to use nitrogen.

Conclusion

The use of nitrogen gas to attain low oxygen content atmospheres for fumigation of museum objects is a feasible alternative to toxic gases. All commonly found museum pests can be eradicated by using a 0.1 % oxygen atmosphere. The systems designed could maintain the relative humidity and oxygen concentration at any desired level. Future mortality studies at higher oxygen concentration will make this method of insect eradication even easier for museums to use.

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Abstract

The purpose of this paper is to review the literature on fungus activity to determine what is relevant to its prevention and eradication on cultural property. The literature shows the need to consider all aspects of the life cycle. Presently used prevention, control, and eradication measures usually consider only the vegetative growth of the fungus. The conidia (asexual spore) activation and germination are precursors to vegetative growth and must be considered in these measures. The literature also shows; that in reference to conidia activation and germination, some conservation treatments may be putting artifacts in jeopardy of future fungi activity and that the absolute moisture content of materials is as important as the relative humidity or their water activity. The information is presented as a basis for discussion, bearing in mind that if humidity and temperature are controlled no significant growth will occur even if spores are activated.

Keywords

Fungus activity, conidial fungi, fungus prevention, fungus, eradication, fungus control, fungi contaminants, air spora, conidia activation, conidia germination, conidia dormancy

Conidial Fungi (Mould) Activity on Artifact Materials—A New Look at Prevention, Control, and Eradication

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Introduction

In the archival, museum, or heritage artifact world, pervasive microscopic and highly obvious fungi activity is not uncommon, i.e., foxing spots on paper and textiles, profuse growth on wet materials, incipient growth on frescoes and paintings, etc. Unfortunately, we respond to these challenges with preventive and active treatments without a thorough understanding of the reason for the fungus activity. The vegetative growth of the fungus is basically all that we consider in our presently used prevention, control, and eradication measures even though conidia (spore) activation and germination are the precursors to vegetative growth (1–3). These aspects of the conidia should be well understood to evolve logical prevention measures.

Fungi reproduce by forming asexual conidia or sexual spores. The fungi, which cause mould growth on surfaces of dead organic materials such as artifacts, produce asexual conidia and it is these conidia which initiate this growth. It is these fungi that are called the conidial fungi.

Conidia are usually spherical, unicellular structures approximately 5–10 μm in diameter and of low metabolic activity. The conidium has both a reproductive and survival function and is the main vehicle of dispersion.

The conidium

The life cycle of common surface-growing conidial fungi, such as the *Aspergillus* or *Penicillium* species, may be divided into a series of sequential stages: conidia maturation, dormancy, activation and germination, thallus growth, and sporulation. The conidia activity is rarely mentioned in discussions of prevention and eradication. All stages are important, but the conidia activation and germination stage is emphasized in this paper. Generalizations can be made from this study, but given the diversity and individuality of fungi, there will undoubtedly be exceptions.

Maturation in conidia is the internal development required to become morphologically and physiological complete.

Sussman defines constitutional dormancy in conidia as the innate state that does not allow germination, even under conducive environmental conditions (4). Dormant conidia are in a metabolically inactive but reversible rest period. Exogenous dormancy is defined as a condition in which development is delayed because of unfavorable conditions.

The following information on conidia activation is from Cotter, Sussman, and Griffin (4–7). Activation of conidia is a process that breaks dormancy and leads to germination. Some conidia or spores are dormant due to adverse environmental conditions and will germinate readily when conducive environments occur that will support hyphal growth. Others, however, will not germinate under conducive conditions and require an activation treatment. The main treatments that effect activation are temperature extremes, drying or wetting, and exposure to chemical activation.

Conidia activation is probably one of the most important aspects of prevention and control of fungi activity but it has been completely overlooked in our present fungal control approaches. All we have to do to convince ourselves of its importance is to look outside on a rainy day. Everything is wet, and according to our simplistic understanding of fungi, all the conidia should germinate and everything should be covered with fungal growth, but this is not the case. The

reason there is no fungal growth is because the conidia have not been activated; therefore, they cannot adsorb moisture and start respiration and germination.

Even if conidia are activated they do not germinate unless there are suitable environmental conditions. Activation may be reversed to dormancy or activated conidia may remain activated for long periods of time before undergoing germination.

The studies of Kowalik and Sadurska and Gallo compared the air spora, those fungi spores and conidia found normally in air, with those that develop on old books and prints (8, 9). They found that the fungi growing on the materials were found in the air but not all of the fungi in the air grew on these materials. The fact that some conidia or spores present on old books and papers did not grow on the materials suggests that they were dormant and would not germinate until activated.

In reference to the purpose of this paper, only the role of temperature and chemical species in conidia activation will be discussed.

Mild heat treatment may activate dormant conidia or spores of some fungal species. This activation remains even if the spores are dried or frozen before germination. Heat activation requires temperatures ranging from 40–75°C for varying lengths of times from five minutes to five hours. Different species require a diversity of durations and temperatures.

It is suggested that heat activation increases mitochondria membrane permeability to non-electrolytes or increases enzyme activity that requires phospholipids or wetting agents for activation. Low temperatures, freezing, or alternating freeze/thaw cycles have also been shown to cause conidia or spore activation.

The conservation implications of this information relate specifically to those collections that are subjected to heat treatment. Herbarium specimens are commonly dried by heat and some treatments on artifacts and paper require heat for surface or adhesive drying. It is possible that short term heating may activate fungal spores already on these objects or specimens and, if in the event of a disaster in which they are exposed to excessive water, the spores might germinate immediately.

Freezing dry artifacts for insect eradication is a common treatment. Tests are being undertaken by the author to determine if in fact this causes activation of spores on such materials which would make them more vulnerable to fungal activity if they subsequently become wet.

The literature shows that the following chemicals, many which are used in conservation treatment, activate specific spores or conidia: methanol, ethanol, glycerol, acetone, detergents, Tween-20, amino acids, organic acids (acetic acid, propionic, butyric) and furfural, furans, thiophenes, pyrroles, phenethyl alcohol, phenyl acetaldehyde, phenyl acetate and benzyl alcohol in concentrations less than 10^{-2} M, and organic solvents such as aliphatic alcohols, ketones, and esters in concentrations greater than 1M (14–17). Acid and alkaline treatments, 1% peptone, proline and urea are also indicated as conidia or spore activators.

As mentioned before, because of the great variation in species responses, it is difficult to generalize. The list is long but the chemicals act in just a few ways. They increase the permeability and wettability of the conidial wall and organelle membranes. They may cause plasmolyses effects which enhance water adsorption, may be nutrients for the fungus, or may act as respiration stimulators.

To research the effects of all the possible chemicals on all the species found on artifacts would be an enormous and unnecessary task. However, we can prevent the problem by removing conidia from objects prior to treatment and prevent recontamination. Also, if fungal growth occurs on a specific object, it is interesting to check the treatment report of the object to determine if it could be related to a prior treatment.

The report of increased vulnerability to fungal growth on parchments after ethylene oxide fumigation treatment may be due to small amounts of ethylene glycol, a by-product of ethylene oxide fumigation (now rarely used because of

environmental hazards) and water, which acts as an activator on conidia that fall on the books after fumigation. Empirical observations, such that polyethylene glycol (PEG) treated leather supports fungal growth, may also be related to the role of PEG in spore activation. Even the use of protein grounds, alkaline treatment or detergents may cause spore activation which could lead to excessive conidia germination under high humidity or wetting. Free amino acids, such as proline, or peptides from deteriorated collagen on leather or parchment could act as conidia activators. Alcohols and acetone are used in conservation but the concentrations are usually so high that they act as biocides.

Conidia deactivation occurs with dehydration, low oxygen concentration in the air (less than 2%) which must occur within six hours after activation by pH or temperature changes. Incubation at 0°C results in effective deactivation but does not kill swollen spores. If the deactivated spores are returned to permissive conditions, spore swelling occurs in 10–20 minutes (4). The conservation implications of this relate to wet materials that have been temporarily stored under refrigeration (or frozen to kill insects). As soon as they reach room temperature, rapid fungus activity may commence.

Conidia germination

The germination process, like activation, is not addressed in the discussion of fungal preventive and control methods. Only the vegetative growth that we can see and methods to control the environmental parameters that influence this growth are considered. Conidia germination often goes unseen and only when it appears after subsequent growth as foxing spots are we aware that it has occurred.

Once dormancy is broken, germination begins if there are conducive environmental conditions for hyphae growth. Gottlieb discusses the germination of conidia in detail (10). Germination includes swelling, the formation of the germ tube which is the beginning of a hyphae and thallus, and an increase in metabolic or enzyme activity and respiration. These activities requires the presence in the conidia of a regulatory system, respiratory enzymes, and essential nutrients. The chemical composition of conidia shows the presence of potential nutrients—carbohydrates, lipids, and proteins—but some conidia, even those with oils, require an exogenous source of energy such as carbohydrates. Many conidia are surrounded with a slimy matrix that may act as a nutrient or increase EMC for a given RH. Exogenous nutrients may not always be required for conidia germination but are required for subsequent continued growth. If they are not present, the germinated conidia will die.

The environmental factors that influence conidia germination are temperature, light, oxygen, carbon dioxide, water availability, pH, and the osmotic characteristics of the substrate. Because of the brevity of this paper only the role of temperature and water will be discussed.

Temperature responses are species specific, but in general, germination is limited by minimum temperatures between 0–10°C with a maximum of 34–36°C. The optimum temperature for germination is around 26°C.

The greatest threat from fungal growth comes when artifacts become wet or damp. Storing them wet or damp at low but not freezing temperatures will reduce the rate of growth or germination but will not kill the hyphae. Freezing the germinating conidia and hyphae may kill them (11).

At temperatures of 36°C or above, the conidia may remain viable for a few hours, but then they are usually killed. This information is relevant for the control or prevention of conidia germination. Dehydration at temperature around 36°C not only dries the artifact materials, but also often kills the conidia. Some artifacts can not withstand the high temperatures and should not be dried this way, but drying under physical constraint may overcome some of the problems (12). Freezing wet materials also may not be suitable because of ice damage (13). Freezing is also of questionable effectiveness in killing dry conidia.

Water relationships

There are three aspects to water as it relates to fungal activation and growth: the water vapor of air, the water content of the conidia, and the water content of the substrate. It is difficult to separate the influence of one from another in conidia germination or fungus growth. In the sequence of events of conidia germination, water vapor may be adsorbed from the air by an activated conidium and later from the substrate by the developing germ tube or hyphae.

The water vapor concentration in the atmosphere is measured as relative humidity (RH). This is the ratio of the actual water content (partial vapor pressure) to the saturated content (partial vapor pressure) at that temperature.

The water content of the conidia or substrate (the material of the artifact), in equilibrium with its surrounding atmosphere, is expressed either as a quantitative amount (the equilibrium moisture content or EMC) or as water activity (7, 14–19). The EMC is based on a percentage of dry weight. Water activity (a_w) is expressed as

$$a_w = p/p_0$$

where

p = vapor pressure of water in the conidia or substrate

p_0 = vapor pressure of pure water at that temperature

At equilibrium, relative humidity will have the same value as a_w .

The EMC in the body of a substrate is influenced by the amounts and types of solutes in solution. For example, doubling the content of a given solute in the material will double the amount of water required to meet the a_w and hence will double the EMC. The fungus with its solute content competes across the osmotic barrier of its membrane with the solutes in the substrate for the water molecules it requires for growth. For a given RH and water activity, the EMC of a substrate may be high because of its solutes. The corresponding low water activity in the substrate may not make water available for transfusion across the membrane for enhanced fungal activity.

Life exists over the range of 1.0–0.6 a_w (100–60% RH). Growth of animals is confined to a_w 0.99+; most microorganisms are limited by 0.95 a_w . Practically, the water activity tolerance of fungi falls between 1.00 and 0.55. Growth cannot occur at 1.00 (pure water) without some nutrients and at 0.55, DNA becomes denatured.

During germination, the water activity or EMC in the conidia remains substantially constant, similar to the water content in our own body cells. In dormant conidia or spores, the water activity will change in response to changes in environmental parameters.

Fungi are categorized according to their water requirements. There is confusion in the literature with the terms for these classes. Griffin discusses the problem of categorizing fungi according to their water requirements. Griffin suggests the terms “xerophilic” for those fungi that require low water activity for optimum growth and “xerotolerant” for those that can grow at low a_w but require a higher a_w for optimum growth (7). Xerophylic fungi cannot grow at a water activity of 0.98 or greater and minimum growth occurs at 0.90. Xerotolerant fungi have minimum growth about 0.97.

Pitt defines a xerophylic fungus as a fungus that is capable of growth at a water activity below 0.85 and states that the limit 0.85 has been chosen as an empirical but practical value in food technology (20, 21). In defining xerophylic fungi, he suggests that the terms “halophilic” (lovers of salt), “osmophilic” (lovers of high osmotic pressure), and “xerophylic” (lovers of dryness) are overlapping and imprecise. The interest in xerophilic fungi in this paper is because of the occurrence of fungi growth on what appear to be dry materials, such as paper, causing foxing spots (19).

In the list of 44 known xerophylic fungi, 12 were *Aspergillus*, 14 *Penicillium* and seven *Eurotium*, all ubiquitous species. The remaining 11 included seven different

rare species. The *Aspergillus* species had lower minimum water activity than the *Penicillium* species. The prevalence of these species on archival and artifact materials, suggests that they are present because of their xerophylic nature (2, 19, 22, 23).

Griffin suggests that the mechanism of tolerance to low water activity is due to the production of polyols such as glycerol (7). They act as a osmoregulator in xerophylic conidia which allows them to adsorb and retain large quantities of water that range from 52–72% EMC as compared to other fungi conidia with 6–25% EMC for similar water activities.

The rate of fungi deterioration of dried food in relation to a_w is outlined by Scott (14). "Spoilage of virtually all foods occurs readily within one to two weeks at an a_w of 0.80–0.85 by a large variety of fungi, but, as the a_w is reduced to 0.75, spoilage is delayed and fewer fungi species are involved. At 0.70 spoilage is greatly delayed and does not always occur even after prolonged storage. At 0.65 a_w very few fungi are known to grow and spoilage would be most unlikely to occur in less than one to one-half to two years." The significance of this information relates, in the material of the artifact to the variable a_w , and hence to the RH of the environment. Holding materials at a presumed favorable RH may not protect them all from a variety of fungal activity.

In the literature, tolerance of fungi is often related to RH. Pitt considers 70% as maximum RH to prevent fungus growth and says that if it does occur, it must be due to some microenvironment with a higher RH (21). Compared with Nyuksha's work which follows, he has failed to consider the different EMC of materials (24).

Scott reports that at a given temperature, a reduction in water activity causes a fall in germination rate, an extension of the latent period, and a reduction of the rate of germ tube extension (14). At optimum temperature, the range of water activities supporting germination was greatest. The presence of nutrients increased the range of water activities which supported conidia germination. Substrates of high osmotic forces have a higher EMC but a lower a_w and usually showed lower germination rates.

This is an extremely important aspect of fungal activity that is rarely addressed. Its importance is shown in the work of Nyuksha (24). Since the fungal destruction of fiber material results in more than half of its weight increase in freed water, the accumulation of water by a fungal colony can be largely independent of local RH. Furthermore, "since paper is a very complex hygroscopic system with inhomogeneous capillary properties . . . the manufacturing process . . . establishes the ultimate moisture content," due to colloidal, capillary, or imbibed water. Oxygen permeability can also play a major part. It was shown that five different papers each required a different RH before 8–10% conidia germination occurred. In contrast to the results in the previous research this may indicate that the absolute amount of water in the substrate was the limiting parameter not RH and hence a_w (21). Again, differences in the amount of organic or inorganic solutes in the paper will require different absolute quantities of water to achieve the same a_w . Thus, these results indicate that the absolute amount of water in the materials and not its water activity is the major influence on fungal conidia germination and subsequent vegetative growth. This might explain why many materials become mouldy before others under the same RH and temperature.

The importance of these latter results means that we can not hope to have complete control of all conidia activity by controlling RH. One logical additional element of control is the elimination of sources of fungal spores. Prevention of surface contamination from air spora may be achieved by storing objects in dust-proof containers and covering them at all times when temporarily removed from storage. Preliminary vacuuming, according to conservation standards, of objects prior to storage is logical. Positive-pressure exhibit cases in which the air brought into the exhibit case is filtered for fungi can prevent surface contamination (26). Super-filtration in a room with an air-conditioning system will reduce the conidia load in the air, but will not eliminate it because of conidia brought in from the

outside by air currents through doors and by people. All ancillary materials, such as starch paste, protein grounds, or adhesives, etc., used in wet conservation treatments should be sterilized (23). Also, aseptic techniques should be used; all activities should prevent contamination of materials during treatment. Such measures would include avoiding the use of fans, sterilizing work surfaces and tools, and using a filtered, positive pressure hood for treatments. With all these precautions, fungal spores are so prevalent that, until we know more about activation, only inhibition of growth by climate control, both generally and in discrete localities, will rid us of the vast majority of our problems from overt fungal infestation and growth.

Conclusion

This literature review shows that in designing logical methods of eradication and prevention of fungal activity, all stages of the life cycle of conidial fungi must be considered. Conidia activity and germination must be considered, as well as vegetative growth. Some conidia activators reported in the fungi physiology literature are also common conservation treatments. Empirical observations suggest that these treatments may be putting artifacts in jeopardy of fungal activity.

The most important aspect of maintaining conidia germination and vegetative growth is the absolute moisture content of the substrate (or material of the artifact). Water activity, not only RH, influences the absolute amount of water in objects. This explains why different materials at a specific RH may or may not support fungal activity. Some conservation treatments may alter water activity of materials, and increase the absolute water amount, putting them in jeopardy of fungal activity. Because of the prevalence of fungal conidia, until we better understand activation and germination, we must at least prevent fungal growth and contamination of artifact surfaces. Some measures, such as aseptic technique, dust protection, and air filtering may reduce the amount of contamination. Another preventive measure is environmental control, as it restricts fungal growth.

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Abstract

A project was initiated to determine the most effective means of controlling the biodeterioration of outdoor sculpture and architectural elements at Hearst San Simeon State Historical Monument. Lichen and moss specimens were collected for identification. In a year-long study, eight different biocides were tested at four separate test sites. The biocides were monitored for initial effect, persistence, and interaction with the substrates. In addition, the results of these tests were also correlated with the measured effectiveness of the various biocides after simulated weathering in laboratory controlled conditions.

Keywords

Biocide, lichens, mosses, algae, microbiological, exterior, stone, terra cotta

An Evaluation of Biocides for Control of the Biodeterioration of Artifacts at Hearst Castle

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Introduction

After the death of William Randolph Hearst, his large residence in San Simeon was donated to the State of California in order that it might be opened to the public. The Hearst Monument is located near the Pacific Ocean in a climate classified as Mediterranean (moderate annual temperatures, dry, warm summers and cool, wet winters). The area is subjected regularly to mists which rise from the near shore waters, and to winds which essentially meet no tempering forces as they cross thousands of miles of open ocean unimpeded before reaching the Santa Lucia mountains upon which the buildings are perched.

Exposure to the elements has caused the exterior artifacts at Hearst Castle to become habitats for various forms of life. There is a significant cover of lichens on the vast majority of objects. The encrusting varieties in particular cling intimately to the substrate, obscuring the details and causing visible damage to the surfaces. Mosses proliferate on concrete, and to a lesser extent on terra cotta. Algae are present on stone surfaces as part of lichen thalli.

In order to limit any further biological degradation of the outdoor artifacts and architectural elements, a year-long program was initiated. Specimens were collected for identification from different substrates. Eight biocides were subsequently applied on four exterior test sites, and their performance was monitored over a prolonged period of time. The effectiveness of the biocides after simulated weathering was also evaluated in laboratory tests.

Identification of the microorganisms

The study focused primarily on lichens since they were present in substantially larger amounts than the other organisms. Specimens were collected from concrete, marble, terra cotta and granite, and 23 species from 13 genera were identified (See Table I) (1). Only four were classified as foliose; the others were all crustose. The greatest variety of species (thirteen) and genera (eight) were collected from terra cotta. Mosses were collected and identified as listed in Table I (2).

Interaction with the substrate

Lichens thrive in extreme environmental conditions and indeed often require them to maintain the delicate balance between their two symbionts. They generally need alternating periods of drying and wetting, with wetting as brief as a bit of morning dew sufficient for metabolization.

Lichens interact chemically with the substrate (3,4) (in this case stone, terra cotta and concrete) primarily through the action of common organic acids, most notably oxalic acid. This acid reacts with the material to form poorly ordered gels, iron oxides and calcium oxalate (5). Other organic acids found in lichen are gluconic, citric, usnic and lecanoric. The latter two have the ability to form metal complexes with substrate minerals, and to act as chelating agents to bind metal ions, further accelerating the decomposition of the substrate (6).

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Table I. Lichens and mosses at Hearst Castle.

	tc	m	c
<i>Acarospora fuscata</i>	x		
<i>Acarospora peltastica</i>	x		
<i>Acarospora rufescens</i>	x		
<i>Caloplaca aurantiaca</i>		x	x
<i>Caloplaca bolacina</i>	x		x
<i>Caloplaca cerina</i>		x	
<i>Caloplaca citrina</i>	x	x	x
<i>Caloplaca holocarpa</i>		x	
<i>Caloplaca trachyphylla</i>	x	x	x
<i>Candelaria concolor</i>		x	
<i>Candelariella vitellina</i>	x	x	x
<i>Collema crispum</i>		x	
<i>Dimelaena radiata</i>	x		
<i>Heterocarpon ochroleucum</i>	x		
<i>Lecania brunonis</i>			x
<i>Lecanora atra</i>			x
<i>Lecanora hageni</i>		x	x
<i>Lecanora muralis</i>	x		x
<i>Lecanora subfusca</i>	x		
<i>Phaeophyscia hirsuta</i>		x	
<i>Physconia deterosa</i>			x
<i>Sarcogyne simplex</i>	x		
<i>Xanthoparmelia taractica</i>	x		
<i>Grimmia pulvinata</i>			x
<i>Orthotricum rupestre</i>			x
<i>Tortula princeps</i>			x

tc: on terra cotta; m: on marble; c: on concrete.

With crustose lichens, the chemical alteration of the substrate is quickly followed with hyphal penetration, sometimes to a depth of over 1.5 cm (7). As time passes, the upper surface of the artifact actually becomes separated and incorporated into the thallus of the lichen. This phenomenon was particularly evident at the Hearst Monument in objects fashioned from terra cotta.

Selecting the biocides for testing

The amount of material written on the subject would seem to indicate that humans have long been embroiled in a battle to preserve their structures and artifacts from destruction by microorganisms. Around the world any number of substances and methods have been tried (and/or recommended) for this purpose (8,9,10). After a thorough examination of this literature, and consultation with specialists, we chose to test the biocides listed in Table II. The eight biocides can be characterized with regard to their active ingredients, the agents ultimately responsible for the biocidal activity. All were purported to meet the following standards, although some fell short in one or two areas.

Table II. Biocides tested.

Trade name	Manufacturer	Active ingredient	Concentrations tested
Syn-Cide Plus	Calgon	Quat*	75.%, 3.8%
Totil	Calgon	Quat	1.08%, 0.108%
Ucarcide	Union Carbide	Gluteraldehyde	1.0%, 0.010%
BAK	Med Chem Corp	Quat	0.13%, 0.013%
Preventol GDB	Bayer (Germany)	Quat	conc., 10%
Polybor	U.S. Borax	Borate**	5%
Nuodex-87	Durham (England)	Ammonium Salt***	5%
H-40 (modified)	ProSoCo, Inc.	Organoiodide	conc.

* Quaternary ammonium salts.

** Disodium octaborate tetrahydrate.

*** Dodecylamine salicylate.

1. Sufficient toxicity to lichens, moss and algae.
2. No adverse effect such as staining, etching or dissolving any component of the original material.
3. Prolonged effect (low volatility, low solubility in water, inert to the effect of ultraviolet light).
4. Decay products not noxious.
5. Low toxicity to humans and other plant life.

Quaternary ammonium salts are classified as detergents, having a hydrophilic and hydrophobic chemical group on the same molecule (e.g. $C_{14}H_{29}N^+(CH_3)_2C_6H_5Cl^-$). As such, they are capable of infiltrating and disrupting the structure of the cell membranes in living organisms, causing the leakage of intracellular materials. The active ingredient in Ucarcide is gluteraldehyde $[OCH(CH_2)_3CHO]$. Aldehydes inactivate cells by alkylating proteins and cross-linking them (11).

The active ingredient in Nuodex-87, dodecylamine salicylate $[CH_3-(CH_2)_{10}CH_2NH_3^+O_2C-C_6H_4-OH]$, combines the biocidal activity of a cationic detergent with the phenolic activity of the anionic portion. Phenolics kill cells by disrupting the plasma membrane and inactivating intracellular proteins and nucleic acids.

The active ingredient in H-40 [modified] (also known as H-40 Plus) is iodine, an organohalogen compound. Halogens are very reactive with cellular components or produce powerful oxidizing agents which react with various parts of the cell. Iodine irreversibly inactivates many cellular proteins by changing their secondary and tertiary structures (12).

Disodium octaborate tetrahydrate $[Na_2B_8O_{13} \cdot 4H_2O]$ is the active ingredient in Polybor. It is unclear how this compound reacts with living tissue.

Evaluating the effectiveness of the biocides

Four test sites were used to test the efficacy of the biocides and to observe the interaction between them and the various substrates. These sites were divided into plots whose lichen populations were approximately equal in amount and species configurations. Each plot was then sprayed with a particular biocide,

Table III. Biocides applied to lichens and mosses at test sites.

Test site/ substrate	Lichens/mosses at the site	Biocides tested
I Horizontal concrete slab	<i>Caloplaca aurantiaca</i> , <i>Caloplaca holocarpa</i> , <i>Caloplaca laeta</i> , <i>Candelariella vitellina</i> , <i>Lecanora hageni</i> , <i>Sarcogyne symplex</i> , <i>Verrucaria</i>	Syn-Cide Plus, Totil, Ucarcide, BAK, Preventol GDB
II Chert rock	<i>Acarospora schleicheri</i> , <i>Caloplaca bolacina</i> , <i>Candelaria concolor</i> , <i>Dimplelaena radiata</i> , <i>Heterocarpon ochroleucum</i> , <i>Lecanora gibbulosa</i> , <i>Physcia albinea</i> , <i>Xanthoparmelia cumberlandia</i> , <i>Xanthoparmelia mexicana</i> , <i>Bryum argenteum</i>	Syn-Cide Plus, Totil, Ucarcide, BAK, Preventol GDB, Polybor, Nuodex-87, H-40 [modified]
III Horizontal marble	<i>Caloplaca aurantiaca</i> , <i>Caloplaca trachyphylla</i> , <i>Candelariella vitellina</i> , <i>Lecanora hageni</i> , <i>Phaeophyscia hirsuta</i>	Syn-Cide Plus, Preventol GDB, Polybor, Nuodex-87, H-40 [modified]
IV Horizontal & vertical concrete	<i>Caloplaca aurantiaca</i> , <i>Caloplaca bolacina</i> , <i>Caloplaca citrina</i> , <i>Lecania brunonis</i> , <i>Lecanora atra</i> , <i>Lecanora hageni</i> , <i>Lecanora muralis</i> , <i>Physconia detersa</i> , <i>Grimmia pulvinata</i> , <i>Orthotrichum rupestre</i> , <i>Tortula princeps</i>	Syn-Cide Plus, Totil, Polybor, Nuodex-87, H-40 [modified]

including a control area sprayed with deionized water. The lichens, mosses and the substrates were periodically observed and the organisms were examined microscopically for signs of death and deterioration. We used the absence of chlorophyll in the algal layer as the main parameter to indicate the death of a lichen, because as many as 18 months must often pass before the dead thallus physically deteriorates (13).

The lichens and mosses identified at each test site as well as the biocides applied are listed in Table III. The efficacy of each biocide was rated on a scale of 0–4, with 0 indicating no change in the growth, and 4 reflecting a complete absence of chlorophyll (See fig. 1).

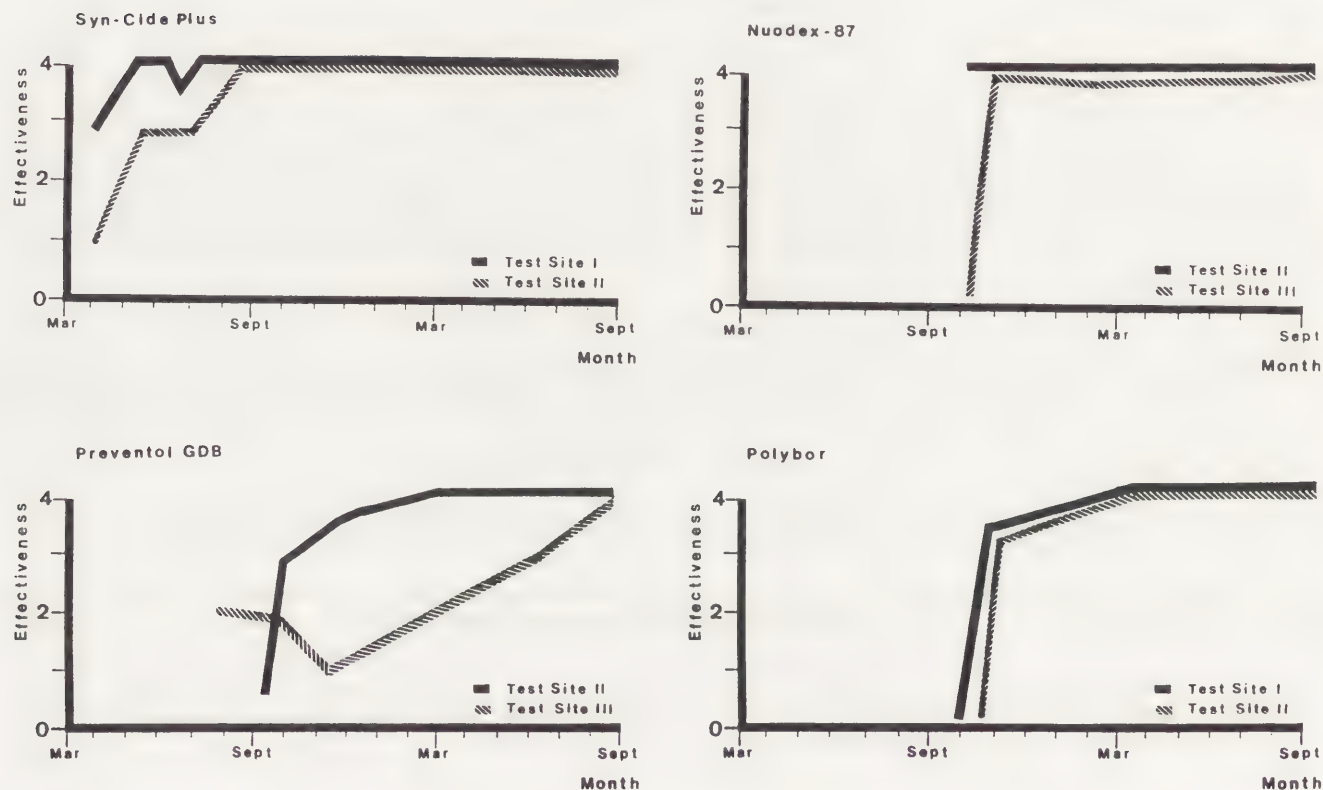


Fig. 1—The relative effectiveness of the four biocides which performed best in tests on lichens.

Algal bioassay experiments

In addition to the outdoor test sites utilized for the lichen studies, a series of bioassay experiments was devised so that the efficacy of the biocides could be evaluated within laboratory controlled conditions. Because of the extremely slow growth rate of the lichens, algae were used in these experiments (See Table IV). The methodology used derives from the work of Grant and Bravery (14, 15). Plastic boxes were washed and rinsed thoroughly. Sterile vermiculite and deionized water were added to each box. Marble slabs (10 × 10 × 2cm), washed and soaked in deionized water and dipped briefly in nutrient agar solution, were placed one in each box on top of the vermiculite. The slabs were inoculated with a mixture of algae and cyanobacteria suspended in a nutrient broth. The boxes were covered and placed under grow-lights with a 16 hr. day. Four weeks later the slabs showed vigorous growth.

Table IV. Bioassay organisms.

Chlorophyta:

Trebouxia
Stichococcus
Chlorella
Protococcus

Cyanobacteria:

Gloecapsa
Calothrix

Bioassay experiment # 1 (concentration comparison)

Thirty days after inoculation, four biocides (BAK, SynCide Plus, Totil, Ucarcide) were applied to the slabs, each in two different concentrations. The concentrations were the same as those used in the lichen experiments (see Table II). One control slab was sprayed only with deionized water. Four weeks later the growth of algae on each slab was evaluated. Algal growth was rated on a scale of 0–4, with 0 representing no sign of life and 4 indicating growth equal to the control slab. Viability was determined utilizing incidental light and UV-fluorescent microscopy, and vital staining with tetrazolium salts (16, 17). In order to test

the residual effects of the biocides, the slabs were reinoculated and observed again at four weeks and six months later (See fig. 2).

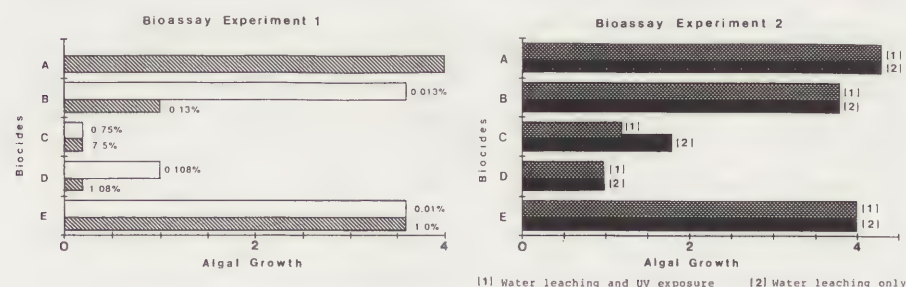


Fig. 2—Bioassay Experiment #1 compares two concentrations for each of four biocides (A—deionized water; B—BAK; C—SynCide Plus; D—Totil; E—Ucarcide), monitoring their effectiveness up to 22 weeks after their initial application and 18 weeks after reinoculation. Bioassay Experiment #2 compares the persistence of four biocides four weeks after exposure to simulated weathering conditions. (A—Concentrated H-40 [modified]; B—5% Nuodex-87; C—5% Polybor; D—10% Preventol GDB; E—deionized water).

Bioassay experiment # 2 (artificial weathering)

This experiment tested the persistence of four biocides (H-40 [modified], Nuodex-87, Polybor and Preventol GDB) which were purportedly effective for prolonged periods after the initial application. The biocides were again tested in the same concentrations as those in the lichen experiments (see Table II). Four weeks after inoculation, each biocide was applied to two test slabs and two control slabs were sprayed with deionized water. Three weeks later, the green growth on the slabs was rated and all of them were then removed from the boxes for simulated weathering. One slab for each biocide was placed in a Pyrex dish where 17.5 liters of deionized water was recirculated over it for 24 hours at the rate of 5.65 liters per minute. The remaining slabs were exposed to ultraviolet light for a 60-hour period under a bulb which simulates four times the severity of sunlight. Both groups of slabs were then reinoculated and evaluated for new growth four weeks later, utilizing the same methods previously described (See fig. 2).

Conclusions

Four biocides (Nuodex-87, Preventol GDB, Polybor and SynCide Plus) demonstrated the highest toxicities. Of these, Nuodex acted the most quickly. Biocidal activity persisted best after weathering in Preventol GDB and somewhat in Polybor. Although SynCide Plus is highly soluble in water, it gave some indication that its biocidal capabilities will persist over time. Negative characteristics exhibited by these four top performers include a poor persistence in the weathering experiment by Nuodex-87, the toxicity of Polybor to higher plants, and staining of the substrate by Preventol GDB when applied in the higher concentration. During this project, we observed only one instance of damage to a substrate which occurred as the result of application of a biocide. This was the staining of the surface caused by Preventol GDB. Further studies on uncontaminated substrates are being carried out in order to determine whether any physical alterations of the surface (e.g. staining, efflorescence, etching) can be observed under microscope after repeated applications of the biocides.

SynSide Plus was tested more than any other biocide in order to gain information on a range of concentrations. There was virtually no effect at 0.45%, but both 3.8% and 4.5% were very efficient. It appears that hotter weather accelerates and perhaps intensifies the process. Due to the water-soluble nature of SynSide Plus, it was not tested in the simulated weathering experiment. However, contrary to expectations, there was no decrease in efficacy observed in the post-winter months after the rainy season had passed, and it persisted in Bioassay Experiment #1. Because there was little rain during the test period, we cannot be certain whether the solubility of this biocide will produce diminished efficacy in areas where rainfall is more extensive.

Totil (1.08%) showed excellent toxicity to mosses but only moderate effect on the lichens, particularly within the first three months after application. Bioassay Experiment #1 indicated that it retained toxicity satisfactorily.

Ucarcide was proved ineffective at a concentration of 0.01% (which was utilized in an attempt to examine the lower possibilities of effective biocide strengths). The 1% solution showed an initial low response, but increased to moderate efficacy during the hotter summer months. BAK was the least active of the biocides tested. It showed very low toxicity to lichens in the field at both concentrations, and very low toxicity in the bioassay experiment. We were unable to compare it at 1% because it was only available to us in a commercially prepared solution of 0.13%.

Preventol GDB demonstrated moderate to high toxicity to lichens and fairly high toxicity to mosses and algae. It also maintained its biocidal activity well after simulated weathering. A significant problem with Preventol is its staining of the substrate, particularly in higher concentrations. At present, it is unavailable for distribution in the United States.

Polybor demonstrated high toxicity to lichen and moss. Toxicity was sustained quite well after water leaching and UV exposure. The decision to use this biocide should be made with the understanding that its soluble alkali metal salts can accumulate in the fabric of the substrate, causing significant crystallization and damage to the surface by spalling.

Nuodex-87. Out of all the eight biocides, the lichens responded most rapidly to Nuodex-87. A drawback to this biocide, however, is that it lost most of its capabilities following the simulated weathering processes of water and ultraviolet light exposure.

H-40 (modified) demonstrated fair to good toxicity to lichens and moss, but the results of the simulated weathering showed an increase of algal growth when compared to the control sample. This may be due to our method of application which was spraying, rather than the dipping specified by the supplier. However, since in most cases the size of an object prohibits dipping, these results are pertinent.

Recommendations

Based on the test results, we recommend two sequential treatments for the eradication of lichens. The first involves the application of a solution of 5% Nuodex-87 in water. This showed good, rapid, results and yet it did not stand up to the simulated weathering. The initial application should therefore be followed, three months later, by a 7.5% aqueous spray of SynCide Plus, which was slower acting but most effective over time.

A 1% aqueous solution of Totil is suggested for the eradication of mosses. Both 7.5% and 0.75% SynCide Plus solutions were shown to be very active on algae. Since algae commonly appears after lichen removal, the Nuodex-87 or SynCide Plus treatments used to eradicate the lichen will generally suffice to deter algae growth.

We suggest that the initial treatment should be made during the summer months, when higher temperatures and less precipitation allow the biocides to work at maximum effectiveness. The solutions should be sprayed over the growth until thorough saturation is achieved. The nozzle of the sprayer should be adjusted so that a moderate (as opposed to a fine) spray is utilized with overlapping, horizontal sweeping motions appearing to be most effective. The foliose lichen and mosses should be examined closely to be sure that the spray has penetrated to the substrate. The viability of any microbiological growths should be determined for 9-12 months following the initial application.

Safety precautions should be scrupulously followed. These include wearing protective clothing, gloves and goggles prescribed by local safety ordinances; utilization of a respirator, fitted and prescribed according to local codes, of the type that protects against fine mists during the entire application period; undertaking no spraying in windy conditions; and taking thorough showers (in-

cluding the washing of hair) for all personnel immediately at the completion of the application.

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Abstract

Use of reactive chemical methods to control insect degradation of cultural property poses significant risk of collateral damage to the object. Safer methods using inert gases such as argon have been implemented at the Metropolitan Museum of Art. A significant gap in knowledge exists between the applicability of treatment times as derived from studies on insects *in vitro* to actual treatment time lengths for insects *in vivo*. Insects *in vivo* or in objects are acclimated to their environment and may be in a number of different physiologically susceptible states (more than may be represented by *in vitro* studies). A technique utilizing Fourier transform infrared spectroscopy has been used to measure insect gas by-products. The method shows promise for non-destructively assessing insect activity before and after treatment and for establishing necessary length of treatment times for objects.

Keywords

Insect eradication, fumigation, Fourier-transform infrared analysis (FTIR), carbon dioxide (CO₂) respiration, argon, nitrogen, inert gases, controlled atmospheres

Insect Eradication Using Controlled Atmospheres and FTIR Measurement for Insect Activity

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Introduction

In the past twenty-five years in the United States, a succession of insecticides has been employed on art objects. However, each, in turn has been found to have been deleterious to the object and/or to personnel handling the object. These insecticides have included methyl bromide, ethylene oxide and, most recently, sulfuryl fluoride (1–4). Research efforts by a number of individuals and organizations over the past few years have focused on alternative, generally non-chemical, treatments (5, 6). Treatments in this category, which can be termed environmental manipulation, have all attempted to control one or more of the essential environmental parameters necessary for insect pests to maintain themselves. Such environmental parameters include temperature, moisture, and atmosphere. The theory implicit in all these studies is that alteration of one, or preferably two or even all three of these parameters will put sufficient stress on the insect at every stage of its life cycle to cause the eradication of the pest. Equal to the goal of neutralizing the insect vector is the goal of not altering the form or substance of the art objects in museums.

Inevitably, it seems, the most effective means for pest control are also the ones most likely to cause an alteration in an art object. For example, using slightly higher temperatures than ambient is often an effective method of killing insects, yet this same temperature elevation may soften components of the art objects, causing them to flow and perhaps increasing the rate of oxidation and dehydration of the objects. Freezing temperatures, on the other hand, while also an effective means of killing insects, may cause a variety of problems. The obvious type of problem is ice crystal formation. More subtle problems are material fatigue from expansion and contraction caused by cooling and reheating, and brittleness due to the freezing making the object more susceptible to low-frequency vibrations from compressor units found in freezers, or even from handling. (Background vibration "noise" has caused problems within The Metropolitan Museum of Art's (MMA) collection that have resulted in fragments of wooden objects completely detaching from the objects. The results of research in this area will be published in a future paper.)

Alteration of moisture conditions (generally toward a drier condition) even if effective in killing insects, tends to be avoided within museums. Since many organic museum objects may crack if subjected to an excessively dry climate, museums in North America and Western Europe usually attempt to stabilize exhibition and storage conditions at approximately 40–50% RH (7).

An environmental manipulation that is benign to the object, and yet will effectively (albeit slowly) kill insects involves the use of a low oxygen atmosphere, specifically, the use of argon, helium, or nitrogen.

The use of nitrogen for pest control is not new. Perhaps the earliest mention of its use was in the 1860s (8–10). Since the 1960s, many studies have been performed using nitrogen to control insect pests in grain storage silos, with notable success (11, 12). Studies on the use of inert environments in museum settings have blossomed over the past five years (13–24).

Recent research has indicated that argon may be 25–50% faster at killing insects than nitrogen (21, 24). Argon's potentially faster eradication rate, chemical inertness, and ability to stratify has made it the gas of choice for our tests.

Details of the procedures employed at the MMA are published elsewhere (18). A summary of the procedure is given below.

Environmental control parameters

Resistance of insects to a low-oxygen environment varies considerably, not only from species to species, but also with life-cycle stage—egg, larval, pupal, or adult—and with age within each cycle (11, 12, 25). Other factors, such as isolation deep inside an object, may also alter the apparent resistance to treatment by an insect at a particular life-cycle stage. Low oxygen levels in the range of 0.1%, achieved with nitrogen, may produce 93–100% mortality rates in 14 days (at 26.7°C) for *Tribolium* spp., flour beetles; and in 21 days for *Tineola bissilliella* (Hummel), webbing clothes moth; *Lasioderma serricorne* (Frabicus), cigarette beetle, *Stegobium paniceum* (Linnaeus), drugstore beetle, and *Anthrenus vorax* (Linnaeus), carpet beetle, at 30°C (26, 15). Higher temperatures generally produce higher mortality rates; lower humidity levels also produce higher mortality rates (27).

Initial length of treatment in the MMA tests was patterned after Navarro, in that the most conservative estimate of length of time was used for the most tolerant life stage of the most tolerant insect (tested thus far) (11). Navarro suggests that *Trogoderma granarium*, kharpa beetle, is the most tolerant insect for grain storage problems, requiring 20 days to kill all stages. This insect is similar in tolerance to those reported by Gilberg (15). Testing and development work have been reported elsewhere (18). The system currently in use is described below.

The most successful system developed at the MMA thus far, in terms of the ease of maintaining a low-oxygen environment, is the pouch or bag method. In this technique, the object is placed in a pouch made of heat-sealable, low-oxygen, permeable plastic (e.g., P869, a co-extruded EVA/nylon/EVA side seal pouch 44" × 90" in size, 3.0 mil thick, from the Cryovac Div., W.R. Grace Co., Simpsonville, SC, U.S.A. O₂ permeability of 30–50 cc/day/m² at 20°C and 1 atmosphere). The oxygen environment inside the bag is flushed out with humidified inert gas to less than 0.1% O₂. An oxygen scavenger and oxygen indicator (Z-2000 AGELESS® and, AGELESS EYE® indicator, respectively, Mitsubishi Gas Chemical America, Inc., 520 Madison Ave., New York, NY, U.S.A.—products available through Cryovac) are placed in the bag and the bag is heat-sealed. The oxygen scavenger functions to absorb any oxygen that diffuses out of the object or leaks into the bag. (A note of caution: the scavenging action of the Mitsubishi AGELESS involves an exothermic reaction process. The higher the oxygen level in the bag, initially or due to leakage, the more reaction heat that will be produced by the scavenger. The scavenger should not be placed on or near delicate art surfaces.) The O₂ indicator provides a quick passive monitoring method to ensure that O₂ levels within the bag are maintained at the desired level (≤0.1%). Measurement with an oxygen meter is performed upon filling the bag, and repeated periodically during the treatment. Measurements are taken from a top surface, as this has the highest oxygen level (since argon is heavier than oxygen). Measurement with an oxygen meter is highly recommended.

An alternate and less oxygen-permeable bag system using BDF-2001 film (1 mil thick. Cryovac Division, W.R. Grace, Inc.) has also been employed. The leakage rate of this type of plastic is ≤5.0 cc/day/m² at 20°C and 1 atmosphere. This system is ideal for smaller objects and for measuring insect respiration by-products.

The pouch systems are portable, inexpensive, quick to set up, effective, and reusable. They can be used for successively smaller objects, provided the sides of the bag have not been pierced.

Insect respiration

Published time-of-treatment data to-date is based upon either isolated insects or recent infestation in non-museum objects. While it may prove reasonable to project time-of-treatment results from these studies to the actual infested object,

there is still some doubt as to the effectiveness of the treatment on real objects. Insects in objects are well acclimated to their niche and may be physically isolated from the environment (e.g., plugs in the holes) in addition to being in different physiologically susceptible states (one to seven distinct instars or larval stages, pupal stages, or the adult stage). Studies by Navarro and others have shown that different insect life cycle stages respond differently to inert gas treatment (11). In practice, it is not always easy to determine if an object is infested, let alone identify the life cycle stage of the insect residing in the object.

Efforts have been made to non-destructively assess the presence and absence of insects in materials using a variety of methods. These have included sound waves, X-rays, chemical reagents, microwaves, and nuclear magnetic resonance (28). All of these techniques, with the possible exception of sound waves, would generally be impracticable or even dangerous for use on art objects.

The most promising current technique for non-destructive testing of insect (and any biological) presence is to detect for gaseous by-products. This could include detection of methane (for termites or wood microbes) or carbon dioxide (for insects or microbes). Insect respiration may produce on the order of microliters/minute, or less, of CO_2 . This may represent a 2–3 parts per million (ppm) addition to the "background" level in the atmosphere (about 300 ppm). In order to differentiate respiration from background, a suitably sensitive system has to be employed. Such a system to identify hidden insect infestations in cereal grains has been constructed and tested with a high degree of success (28, 29).

Initial tests demonstrated the ability of the system to detect a CO_2 output of about 1 ppm/min from a rice weevil in 350 g of red wheat (29). Further tests were undertaken comparing the CO_2 -Fourier transform infrared spectroscopy (FTIR) detection capability with standard visual observation techniques practiced by the U.S. Agricultural Research Service and U.S. Federal Grain Inspection Service to determine insect infestations of field-collected samples of wheat (30). The results were quite promising for the new technique; visual detection found that 11% (66 of 597 samples) of the samples were infested, while CO_2 -FTIR respiration showed that 81% (373 of 459 samples) were infested. Follow-up studies by X-ray and incubation of the samples showed that CO_2 -FTIR data correctly detected an infestation in 98% of the samples (368 of 373 cases).

Identification of insect infestations within museum objects is also difficult to recognize, as experiences at the MMA have shown. (*Cryptotermes* sp. powder-post termites from Florida or the Bahamas have been present in our collection from at least 1977, with occasional sighting—we are now undertaking a major effort to locate all infested pieces.)

In an effort to improve our ability to identify when an object is infested and measure the effectiveness of our suffocation treatment, we have developed a modified CO_2 -FTIR respiration system patterned after Bruce and Street (30).

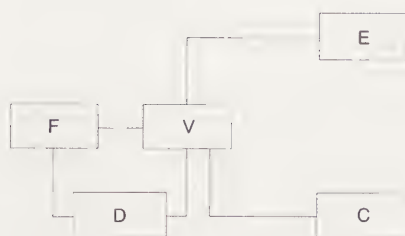


Figure 1. Schematic of FTIR system for measuring insect respiration includes the following: a fixed path length, single-pass cell (F), optimized to measure CO_2 and mounted in a Bomen-Michelson 100 FTIR; a valving system (V); experimental bags (E); control bags (C); and the computer for control and data reduction (D).

FTIR system

The equipment tested at the MMA (See schematic in fig. 1) included an ambient temperature 25-cm single-pass cell with a fixed pathlength, (F), optimized to measure CO_2 , mounted in a Bomen-Michelson 100 FTIR; a valving system (V); and a DOS-computer for control and data reduction (D). (The system was custom built by Sprouse Scientific, Inc. 19 E. Central Ave., Paoli, PA 19301.) The absolute sensitivity to CO_2 is in the 0–50 ppm range; Bruce and Street, with a similarly sensitive device, were able to detect a 1 ppm/min change of CO_2 from 1 insect living in 1 grain of cereal in about a ½-liter volume (29).

Our initial design utilized separate control and experimental bags. Control test runs showed that the system could reliably detect an increase in CO_2 of 10 ppm; below that value the variability in sample collection and the instrumentation masked any increase in CO_2 . The system was tested using approximately 10 subterranean worker termites (*Reticulitermes* sp., in wood fragments). Measurements were taken over several weeks, in separate 2–3 day runs. In each case, a steady increase in CO_2 level was easily detected over the course of the test. After establishing the instrument variability and detection sensitivity with known

insects, tests were conducted on a suspected infestation in an easel painting frame. The results, over five days of measurements, showed a steady increase in CO₂ in the bag containing the frame. The experimental bag was then flushed with humidified argon until the oxygen level was below 0.1% (1000 ppm) and new CO₂ measurements taken. No CO₂ was produced in the anoxic environment. After 16 days, the argon was flushed out and the bag was filled with the normal mixture of laboratory air. CO₂ measurements were taken over the next 11 days to detect any insect recovery. No increase in CO₂ was found. This indicated that either the insects were all dead, or that they had not recovered after 11 days in air.

Further testing is underway to define the limits of detection of the instrumentation, such as how a few insects can be detected, in how large a volume, and the length of time data must be collected in order to determine that an object is infested. Testing of the length-of-treatment times is continuing with argon and will be compared to helium, nitrogen, and mixtures of inert gases.

Further refinements to sample collection procedures should permit measurement of lower levels of CO₂. In addition to measuring lower levels of CO₂, the equipment has been modified to enable ppm measurements for methane (produced by bacteria in the gut of termites) as a second method to measure for respiration activity and to aid in identifying the type of insect infestation.

Conclusions

An FTIR system has been successfully modified for measuring low levels of insect-produced CO₂. These measurements of insect respiration permit non-destructive identification of insect activity in an object, demonstrate the effectiveness of inert gas treatments for insect eradication, and permit refinement of length-of-treatment times on eradicating the source of respiration, the insect. Further testing is underway to verify the initial results, develop object-derived length-of-treatment data, measure other relevant gases, and test for the presence of fungal activity.

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Abstract

The stability of fungal cells depends on both the environmental conditions and the state (vegetative cells, conidia, askospores) of their biological structures. An examination of the Kremlin's Armory collection in Moscow established that the museum's storage conditions favored the destruction of fungal spore viability, both in areas where airborne contamination can occur and in areas of previous fungal damage. Mycological investigation of books damaged in a water accident showed a tenfold decrease in the number of viable fungi cells on the leather of book covers housed in those conditions for forty-one months. The observation of fungal populations associated with the accident made it possible to track the stability of the various fungi species. Mechanical cleaning of fungi and subsequent storage of articles in a controlled environment are proposed where well-regulated temperature and relative humidity conditions exist.

Keywords

Humidity, microscopic fungi, dust, spore viability, preservation

Study of Factors Facilitating the Loss of Viability of Microscopic Fungi in Library and Museum Collections

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Introduction

At present there are no efficient anti-fungal fumigants which do not damage materials being treated and which are not toxic for human beings, nor are there any other safe methods of fungicide treatment, including non-chemical ones. The admissibility has been questioned of simple mechanical cleaning of articles damaged by microscopic fungi and subsequent storage of these articles in safe environmental conditions, since viable spores may remain on the articles.

The contamination of museum articles and books by microscopic fungi occurs in various ways. The main source is the air-borne accumulation of fungi cells together with dust. Other sources include the growth of fungi already on articles and equipment if the humidity is increased; the formation of stagnant, humid areas in overloaded repositories, inside the bookcases and in other equipment near the external walls of the building; as well as water-related accidents. In addition, articles purchased for museum and library collections may contain large quantities of viable fungal spores.

Mycologists examining museum and library collections have noticed that frequently spores are not viable on articles showing evidence of old damage by fungal colonies that have not been subjected to cleaning and biocide treatment. At the same time, many fungi are extracted from articles that show no signs of having been contaminated by fungal growth, if these articles are exposed to air-borne dust, are frequently moved from place to place and are in contact with people. At a relative humidity of 50–55% and a temperature of $18^{\circ}\text{C} \pm 1$ degree as recommended for museum, library and archive premises, the fungi on articles are in a state of dormancy. The fungal cells that have accumulated from the air and that get onto the articles as a result of contact and movement, do not undergo activation and stay dormant. The fungal cells formed as a result of local growth, after exhausting the conditions which initially fostered this growth, transfer from an active state to a state of dormancy, which may be accompanied by evidence of damage caused by them.

The stability of microorganism cells is determined by whether or not they have specialized dormant structures (as is the case for various kinds of spores and cysts) and by the depth of that dormancy, depending upon the environmental conditions. The impossibility of any reactions in cells taking place because of the absence of free water and the reduction in the quantity of combined water, causes a state of deep dormancy and, therefore, preserves their viability in the long term. Such a cell state may be produced by various limiting factors, such as low temperature or deep dehydration. There is evidence that microorganism cells can survive in Antarctic ice and in soils left underground for tens of thousand of years (1). This explains the preserved viability of microorganism cells in archaeological finds.

Environmental conditions that border on normal physiological conditions do not facilitate the survival of microorganisms. An investigation of the influence of humidity on microflora in the atmosphere has shown that a relative humidity equal to 50–60% is unfavorable for preserving viability since the microorganisms are in the boundary state between dormancy and metabolic activity (2). From the practical experience of storing microorganism structures, it is known that

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they are preserved badly in normal room conditions unless special methods are used. At such values of relative humidity and temperature, biochemical processes may take place inside dormant cells, and such processes lead to the exhaustion of the cells' energy resources.

Fungal cells are better protected when the fungi develop not only on the surface, but also in the depth of various materials. The fungal cells are more stable in the thickness of materials, for example in a book block, in a stack of archival documents, in canvas folds under the stretcher and under the prophylactic stickers. Within the thickness of books and documents which got wet and thus were cemented into solid blocks and then stored for 35 years in very dry conditions, only a portion of the fungal spores and mycelia preserved their viability. Of 150 inoculations made, in only 44% of the cases growth of fungi began. Besides hyphomycetes, three isolates of basidiomycetes were extracted (3).

Experimental

To study the viability of fungal spores, both in airborne dust and in previously damaged articles, microscopic examination was performed on dust and thin coatings taken from 40 articles. Inoculations were made from the Collection of Cold Steel Artifacts and from the Collection of the Stable Treasury at the Moscow Kremlin Armory onto Czapek-Dox, modified Czapek-Dox, and Sabouraud fungal growth media. From 5 to 15 samples were taken from each article.

Among the articles examined were scabbards for sabres or swords and saddles from the 17th and 18th centuries, made of animal skin using different tanning methods, fish skin, velvet, cloth, silk and wood. Precious metals and colored gemstones were used for decoration. At the Cold Steel Collection, the quantity of dust on the objects was small. Microscopic examination of dust accumulations gave the following results. Besides fabric and skin fibers and various particles of both crystalline and indefinite form, fungal spores were detected of different sizes, colors and forms: non-germinated and at various stages of germination; short growing tube, long growing tube, the beginning of branching, and—in certain cases—the initial stage of mycelium formation. Often the capsules of fungal spores and the walls of the growing tubes were deformed. The beginning of mycelium formation was observed only on the exhibits located in a book-case, in a niche. The small quantity of fungi spores—one or two within the field of vision at $\times 600$ —as well as the diversity of their features indicate that they reached the exhibits along with airborne dirt.

The viability test for the fungal cells showed that the percentage of viable structures within these contaminations was small.

Discussion

During the last several years at the Cold Steel Collection, the RH periodically increased slightly above 60%, with a simultaneous rise in temperature of up to 22–24°C. This allowed the spores to begin germinating since in these conditions the fungi are at the boundary of the stages of dormancy and beginning cell growth. Although these conditions are unfavorable for retaining viability, they cannot be recommended for museum storage, because in this situation limited growth of fungi starts. The loss of viability may occur at lower RH values of 50–60% at the expense of intracellular metabolism.

At the Stable Treasury Collection, parts of exhibits were not subjected to cleaning and conservation for various reasons. Here, besides the dirt on the saddles, fungal colonies were detected in the form of isolated spots or as continuous non-colored thin layers on the leather of saddle trees and flaps. During microscopic examination of samples taken from these areas, large quantities of big, oval, thorned, and sometimes chained fungal spores were observed, but without signs of germination. In several samples of mycelium with deformed walls, conidia were detected belonging to the *Aspergillus* genus. Unlike the fungal colonies, only fungi spores of various morphologies and colors and bacterial cells were detected in the dirt on the skin and fabric of the saddles.

This microscopic examination suggests that only one species of the *Aspergillus* genus was developing on these surfaces. The species of this genus possess maximum stability with regard to low relative humidity, and an increased temperature is optimal for their development. The results of inoculations to the nutrient media indicated that the spores of fungi belonging to the *Aspergillus* genus are not viable. It was revealed that, many years ago, hot water got into the Stable Treasury Collection because of an accident in another room. Since the repository had many objects requiring attention, it was impossible mitigate all the consequences of the accident at once. This resulted in the development of *Aspergillus* colonies on some objects. During the period of more than fifteen years that had passed since the accident, the fungal spores lost their viability in the conditions of museum storage. The humidity and temperature levels in museums do not facilitate prolonged preservation of fungal viability, either within the dirt or in the old contaminations.

The mycological examination of books after the hot water accident in the Russian State Library has shown that the number of viable fungal cells on the book cover leather decreased tenfold after being housed for forty-one months in the room, although the viability still remained very high at 10 million spores per sq.cm. of surface. Species belonging to the *Aspergillus* genus dominated the fungal colonies on the book covers. The most stable species in the colonies was *A. versicolor*, its relative density increasing while the populations of other species were either disappearing or their density was reduced substantially (see Table I).

Table I. Changes in the fungi populations on book cover leather.

Fungi species	Population density, %	
	After the accident	After 41 months
<i>A. ochraceus</i> Wilghelm	29.6	0.6
<i>A. versicolor</i> (Vuill) Tiraboshi	43.9	90.7
<i>A. ustus</i> (Bain) Thom et Church	11.5	0.0
<i>P. chrysogenum</i> Thom	14.0	0.5

* Note: Besides the stated species, 9 other species were detected, but they were represented by solitary isolates.

After three-and-a-half years of storage, other species were detected that had not been discovered immediately after the accident, but their number was low. With the exception of *P. verrucosum* v. *cyclopium*, whose population density was 7.2%, the others were represented by solitary isolates. This may be explained by incomplete identification of fungi colonies in various parts of the book covers. However, the survivability of various species may be tracked by changes in population density for the dominant species.

Conclusions

Taking into account that the storage conditions recommended for museums, libraries and archives cause loss of fungal viability, plus the possibility of recontamination by the fungal spores present in the air and on equipment, the mechanical cleaning of articles contaminated by fungi should be recognized as admissible in certain cases. It would be better to perform the cleaning after drying the thin coating of fungi, preferably using a vacuum, and then to store the cleaned articles in controlled and strictly monitored temperature, moisture and air exchange conditions.

If the temperature and relative humidity in the repository are not regulated or if there is a possibility of deviating from ideal levels even for a short period of time, then treatment with fungicides is preferable.

There also remains the problem of using antifungal fumigants in cases of large-scale accidents to collections, when it is difficult to dry large quantities of materials, and the loss from fungal growth may surpass the loss from the fungicidal treatment.

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1. Specialist Shipmodel Conservation Training at the National Maritime Museum, London, England

Stephen J. Conway, Gillian M. Lewis, Justin McMorro, National Maritime Museum, Greenwich, London SE10 9NF, England

The poster assesses, from the point of view of the intern, the need for specialist training for conservators working with composite collections worldwide, and focuses on a specialist post-graduate internship in shipmodel conservation at the National Maritime Museum (NMM). The complex composite construction and wide range of materials encountered on shipmodels often requires inter-disciplinary consultation. The NMM provides the ideal training situation with internationally renowned collections and diverse professional staff: textiles, paintings, organics, and metals conservators, as well as curators of ship technology. Work was carried out in each of the conservation departments at NMM over a 12-month period and photographs illustrate the various aspects of the intern's involvement. Systems of surveying the collections, including environmental monitoring and control in display, storage, and transit, supported by practical work and research, formed a training package based on the Conservation Unit's guidelines, combining treatments from many disciplines in one specialist field.

2. Training and Research in Conservation: The Royal College of Art/Victoria & Albert Museum Joint Course

Alan Cummings, E. Helen Jones, RCA/V&A Conservation Course, Victoria & Albert Museum, London SW7 2RL, England

The poster outlines the origins, aims, and structure of this course—a collaboration between a national museum and post-graduate college unique in conservation training. The resources offered by these two institutions, combined with those of the University of London's Imperial College, are hard to rival. The course began in 1989, aiming to fill a perceived gap in the training of conservators in some decorative arts disciplines. The program generally leads to an MA by practical work and can take two or three years of full-time study, but it is possible to gain an MA, MPhil, or PhD by research. By involving expert conservators, curators, art historians, and scientists, the course aspires to produce conservators who are highly skilled in their chosen areas of specialization and who have a well-balanced view of the needs and concerns of the profession as a whole. Recent student projects will be illustrated.

3. Recent Student Projects in Textile Conservation

Textile Conservation Centre, Studies and Research Department, Apartment 22, Hampton Court Palace, East Molesey, Surrey KT8 9AU, England

The three-year course for post-graduates at the TCC leading to the Diploma in Textile Conservation from the Courtauld Institute of Art, University of London, has been evolving since its inception in 1975. Since 1991, students in their final year have undertaken two types of projects instead of one. Whilst one of their projects is still based on an object, the second investigates a problem of broader concern in textile conservation. The poster aims to show both the purpose and success of these two types of projects by illustrating a number of those carried out over the last two years. It also outlines projects carried out by students in their second year to show the building blocks of the final year. The poster is thus relevant not only to debate concerning current textile conservation practice but also to the teaching of conservation across the spectrum.

4. The Brazilian National Press Conservation Department: An Early Attempt at Integrating the Handicapped into the Restoration Field

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To celebrate the International Year of the Handicapped in 1977 and to encourage conservation, the Brazilian Ministry of Justice created a Restoration Division staffed by the handicapped. To make the work space more accessible to the handicapped large, open rooms connected by wide doors were created. Because of the high cost of imported equipment, most items, including low tables, chairs on wheels, and low shelving, were built in-house. Other proposals for low sinks, tilting tables, and replacement of door knobs with push bars proved to be too expensive to construct. In-house training for the handicapped was more successful with workshops and demonstrations serving to familiarize the staff with techniques. The most effective training occurred in work units that consisted of a few individuals whose combined efforts could carry out an entire conservation process, from conserving a document to treating a period book. By 1987 the Division had outgrown its location and was moved into the National Press building which has wide corridors, elevators, and ramps to connect its four floors. Due to current high inflation in Brazil, the Restoration Division staff has been cut and services curtailed. In addition, most of the handicapped individuals who started with the Division have left because of low salaries. A few have started their own private conservation practices.

5. European Confederation of Conservator-Restorers' Organizations

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6. The Influence of Ethylene Oxide and Gamma Radiation on the Aging of Paper

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The European Confederation of Conservator-Restorers' Organizations (E.C.C.O.) is the only European Confederation unifying associations of conservators and restorers who have as their principal aim the promotion of the highest professional standards. Together it may be possible to ensure that conservation-restoration is regarded in a truly professional light and that this profession is given the status that it is due within Europe. The poster presents the history of the Confederation as well as its purpose, objectives, membership, and activities.

An alternative to treatment of infestation with ethylene oxide is gamma radiation. The use of ionizing radiation, gamma, roentgen, or beta, for decontaminating objects of cultural value has certain advantages. Radiation can be applied in a clean, quick and simple manner, but the negative effects upon materials constitute a big problem. Insofar as is known, the dose that is necessary to kill micro-organisms causes damage to materials containing cellulose, such as paper and textiles. To arrive at a final judgment about the long-term effects of gamma radiation on paper, five different sorts of paper have been investigated. By way of comparison the influence of an ethylene oxide treatment has also been tested. The papers were chosen to represent the composition of an archive in the Netherlands. For such research one has to rely on new paper; however, to get an indication of the effects on old paper, the General State Archives in the Hague provided a quantity of paper which is roughly 100 years old. The papers being investigated were aged for 3, 6, 12, and 24 days using two different aging methods. In this way, insight was gained into the steepness of the aging graphs and the effect of the two methods upon the aging process. The results of the physical investigations, folding endurance, burst strength, and tear strength, show similarity. The aging process develops in the same way for both 'wet' and 'dry' aging, but the process is faster with 'dry' than with 'wet' aging. In the first stages of aging a relatively fast degradation occurs, expressing itself in a steep curve. After the first three days of the aging process, the curve levels off and the decay is slower. The treatment with gamma rays, however, has an important negative influence upon the physical and chemical properties of the material. The general trend is that during the initial stage the curves are much steeper, but at a later stage in the aging process they run parallel to the paper which has not been treated, although at a considerably lower level. A radiation with 10 kGy gamma rays for 1 hour accelerates the aging process 50% to 100% (dependent on the sort of paper). The acceleration of the aging process takes place chiefly in the initial period of aging. This will have a recurrent, cumulative effect with each new radiation. From the results of the physico-mechanical and chemical investigations of all paper sorts fumigated with ethylene oxide, it appears that there is no effect on the aging process of paper. From some results it might even be concluded that there is a slight positive effect.

7. L'effet des polluants atmosphériques sur le vieillissement accéléré des matériaux celluloses

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Un vaste programme d'études intitulé "Science et Technologie pour la Protection de l'Environnement (STEP) a été engagé par la Communauté Européenne. Il couvre neuf axes de recherche dont l'un consacré à la protection et à la conservation du patrimoine culturel européen. Dans ce cadre, le C.R.C.D.G. participe à une étude sur l'effet de la pollution sur le papier qui se déroule sur trois ans et est réalisé avec la collaboration de trois organismes européens: le Nederlandse Organisatie voor Toegepast (TNO), coordinateur du projet (Pays Bas), le Swedish Pulp and Paper Research Institute (STFI)(Suède), l'Université de Göteborg (CTH)(Suède). L'objectif est d'étudier le processus d'acidification des papiers sous l'effet de la pollution atmosphérique ainsi que les moyens d'y remédier. A cette fin, certains paramètres (gaz employés, température, humidité relative) ont été définis pour refléter au mieux les mécanismes de vieillissement naturel. Des papiers anciens et modernes sont ainsi vieillis artificiellement et leur comportement est étudié en mesurant leur résistance mécanique et leurs caractéristiques chimiques et optiques afin de suivre les réactions d'oxydation et d'hydrolyse de la cellulose. Parmi ces méthodes signalons, entre autres, la spectroscopie infra-rouge à transformée de Fourier (TNO), la diffractométrie de rayons X (C.R.C.D.G.), la microscopie électronique à balayage couplée à l'analyse

X, l'ESCA. Le C.R.C.D.G. assure une partie des vieillissements artificiels dans son simulateur de pollution et s'attache à comparer, à l'aide de ce type de vieillissement, trois méthodes de désacidification de masse (Weit'O, DEZ, et le procédé FMC) afin de déterminer le procédé le plus efficace. Le panneau d'affichage présente un schéma de l'installation de pollution et les conditions de vieillissement adoptées, quelques résultats sur l'évaluation visuelle de trois méthodes de désacidification de masse testées ainsi que quelques données sur le comportement physico-chimique des papiers traités.

8. La restauration de deux dessins de grand format, représentant des arbres généalogiques, peints à l'encre et sépia sur papier

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La restauration de deux grands dessins, l'un du début du XIX^{ème} siècle et l'autre de Viligiardi (1934), représentant deux arbres généalogiques de la Famille Chigi Saracini (collezione Monte dei Paschi di Siena) s'est révélée très délicate et problématique à cause des facteurs suivants: la très grande dimension des objets (4m × 3m), la fragilité du papier due à l'exposition directe et prolongée à la lumière du soleil, l'acidité de l'encre métallurgique du dessin le plus ancien et sa sensibilité à l'humidité. Ces facteurs négatifs réunis sur les mêmes objets nous ont obligés à éviter tout contact direct avec l'eau et l'humidité pour le dessin à l'encre et à le limiter pour le dessin au sépia. Au cours des opérations de restauration, la nécessité d'utiliser une grande quantité de matériel, et notamment de Klucel G (R), nous a exposé au problème du suivi de la composition des produits chimiques du commerce. En effet, nous avons rencontré différentes réactions du Klucel G (R) provenant de deux achats différents. Cette expérience nous a amenés à espérer qu'un contrôle régulier sur les produits les plus utilisés en restauration soit effectué par les instituts de recherches et d'analyse du patrimoine et que ces résultats soient publiés dans les revues internationales et nationales. Certains efforts ont déjà été faits mais, en l'absence d'une action systématique et programmée, ils n'ont qu'une valeur relative.

9. Red, Green, and Yellow/Brown Glazes on Baroque and Rococo Polychromed Sculptures from Minas Gerais, Brazil

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This poster presents some of our recent findings concerning the use of glazes on gilding and silvering surfaces of wooden polychromed sculptures. These preliminary results are part of a major research project designed to study the evolution of the technology of baroque and rococo polychromed sculptures in Minas Gerais. Our methodology includes historic research and scientific analytical techniques such as FTIR, PLM, UV/VIS spectroscopy, SEM, and GC/MS in order to identify the materials and techniques used in Minas during the eighteenth century. We are primarily focusing our attention on the Mother Church of Our Lady of Conception in Catas Altas, Minas Gerais, because its internal decoration is incomplete and the church has never been restored, allowing us access to original materials and techniques dating back to 1738. The green glazes are generally applied over silvering and contain only copper resinate or copper resinate and madder. The observation of the green glaze fragments by PLM allows us to verify the presence of verdigris crystals inside the glaze layer, which suggests that the glazes were immediately applied after the mixture of verdigris and the terpenic resins. The yellow/brown glazes are not yet identified. The red glazes are more interesting because they are composed of an organic yellowish matrix containing several particles of madder lake and wheat starch. As far as we know, this is the first time that analytical results confirm the use of madder lake and wheat starch as components of red glazes over gilding. The technique of adding starch when preparing red lakes is described in the Paduan and Brussels manuscripts (Merrifield, 1849) and also in some Portuguese texts from the eighteenth century, but so far had never been positively identified in samples.

10. Restoration Problems of Painted Egyptian Wooden Objects

Petronella Kovács, Hungarian
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H-1450 Budapest, Hungary

The first Egyptian objects to be brought to Hungary were collected by historians, travellers, and merchants from the 16th through the 18th century. These were preserved in private, church, and state collections. The first restorations of Egyptian wooden objects were carried out in the 1930s for the first permanent exhibition of Egyptian objects in the Museum of Fine Arts. After the second World War, damages incurred during the war required restoration. Between 1960 and 1970 many of the coffins were treated in preparation for a new permanent exhibition. The latter restorations concentrated not only on consolidation of flaking paint layers and repair of loose parts, but also on extensive

retouching and inpainting of large areas. The poster presents five case studies illustrating the challenge of minimizing a conservator's intervention when retouching large areas. The Egyptian objects conserved in the last 10 years by the author originate from the Late, Ptolemaios, and Greco-Roman Periods and belong to various collections. A compromise between the wishes of the owner and the ethical approach of the conservator was often required. In the case of the restoration of the coffin from the Late Period, complete aesthetic reconstruction was expected and carried out, while in the case of a Shebti figure only the consolidation of the wooden material and fixing of loose paint layers were performed.

11. Bibles, Battles, and Bygone Days: Conservation of the Polychromed Eccentric Dioramas of C.M. Powell

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Clarence Powell (1870-1945) created his polychromed dioramas as a hobby in almost complete isolation. Cut off from the mainstream artistic movements of the twentieth century, he was a self-trained artist who created art from found objects and household materials. Powell used a broad range of materials including conventional artists' materials such as household enamels, oil paint, and watercolor to decorate wood, pine, or cork, but he also used cotton, sheet tin, steel, commercial carpeting, rope, and cotton balls instead of traditional canvas. In addition he used wire, glass, mirrors, rope, string, stick pins, and scotch tape. Some of Powell's most unusual materials included plant roots and small tree branches. Over a five-year period, twenty-nine dioramas and other objects were conserved to stabilize and prepare them for exhibition. First, before treatment, all objects were inventoried and photographed, and a conservation survey was prepared. Conservation priorities were established for the collection and a conceptual approach was formulated which included fumigation with Thymol and cleaning with resin soaps and Trisodium Phosphate with water. Torn fabric was repaired with canvas inserts and PVA emulsion, loose wooden figures were glued in place with epoxy resin, and inpainting was done with acrylic emulsion paints. Where necessary, the dioramas were reinforced with metal mending plates. Broken glass was replaced with Plexiglass for safety. Respect for the eccentric nature of the objects and their construction played a key role in conserving this unique example of twentieth-century polychromed sculpture.

12. The Kajima Project: The Study of Japanese Buddhist Sculpture at the Museum of Fine Arts, Boston

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This poster illustrates aspects of a project to catalogue and publish the Japanese collection of the Museum of Fine Arts, Boston. Funded by the Kajima Foundation for the Arts in Japan, the ongoing project brings experts in the field to Boston to collaborate in the study of Japanese works of art. The study includes the examination of 80 pieces of Japanese lacquered, gilded, and polychromed sculpture. The purpose of the technical study is to identify methods of construction, materials, and techniques used in manufacture, as well as to establish the condition and subsequent treatment history of these works. Original and restoration materials including adhesives, surface treatments, and metal fastenings are identified using such analytical methods as X-radiography, polarized light microscopy, Fourier transform infrared microscopy, X-ray diffractometry, scanning electron microscopy, wavelength and energy dispersive X-ray fluorescence, infrared reflectography and gas chromatography-mass spectrometry. Three objects are used to illustrate types of information being gathered for this project and some of the questions formulated during our investigation. Examination of *Miroku Bosatsu*, or Buddha of the Future, dated 1189 by Kaikei, raises questions about its present appearance and past treatment history. X-radiographs and cross-sections illustrate the identification of original and restoration materials. Evaluation of materials used to mask the true condition of the surface raises debate about whether or not to remove them and the nature of acceptable surface appearances. Infrared reflectography is used to read the inscription found on the base of the *Jizo Bosatsu*, dated 1322. Radiography and cross-sections are also used in the examination of a celestial being (possibly 11th century) whose authenticity has been questioned.

13. A Retable of Madrid's 16th Century: Process of Execution

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The restoration that the ICRBC is currently performing on the retable of Colmenar Viejo's Parochial Church in Madrid has granted us the opportunity of closely studying the characteristics, techniques, materials, and process of execution of one of Madrid's most important 16th century retables. Occupying the church's apse, it is composed of polychromed sculptures and paintings on wood. The sculptural decoration is by Francisco Giralte and the Toledans Francisco Linares and Juan de Tover, and the paintings by Sanchez Coello, Hernando de Avila, and Diego de Urbina. The exact contribution of each author has not yet been determined with precision. The sculptural part of the retable must have been initiated around 1570 and the paintings some time after 1579, although it seems that it was not concluded until 1583. With this poster we would like to offer an example of the process of technical execution and the materials of this 16th century grand melange and its different phases such as joinery, architectural assembly, carving, painting, gilding, and quilting. The specific technical requirements that appear on most contracts of this period refer to the importance, from the materials viewpoint, of safeguarding the work's longevity (i.e. specifying the type of wood, plaster, or lime). In other cases the contracts highlight a work's splendor and magnificence, specifying more expensive colors or purer gold. Using these documents in addition to our direct observations, we can say that the artists of the time followed contractual requirements quite faithfully.

14. Cleaning Treatments Involving Wet and Dry Techniques

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The poster presents a selection of cleaning treatments which were designed to tackle specific soiling problems. While these may not be considered standard techniques, they illustrate the wide range of problems we encounter and our general approach to cleaning. We aim to balance the sometimes conflicting demands of client expectations with effective cleaning that does not compromise the long-term stability of the textile. The photographs illustrate the following treatments: (1) animal glue coating the front of a 16th century Flemish tapestry fragment, removed using a poultice of warm paper pulp prior to wet cleaning with a non-ionic surfactant. This pre-treatment minimized the need for mechanical action to remove the glue and shortened the wash time. (2) a tangled and soiled fringe, treated with a series of wash baths containing 10% v/v glycerol enabling it to be untangled and straightened. The fringe was thoroughly rinsed using de-ionized water prior to drying. (3) silk damask wall coverings in a London Grade I listed building had become blackened by urban pollution. This greasy soiling was removed using conservation erasures. (4) a treatment carried out in situ, removing graffiti from a 17th century tapestry. Following consultation with the manufacturer of the ink, organic solvents were used successfully to remove this staining.

15. Typical Deterioration Features in 16th to 18th Century Colonial Easel Painting in Peru

Rosanna Kuon, Museo de Arte de
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27, Peru

Colonial easel paintings in South Andean areas are usually found, or kept, in their original sites (cloisters, rural churches, etc.) in very poor condition. Deterioration reaches critical levels and there are recurrent peculiarities that are not often found in other cultural and geographical contexts. Restorers are challenged by the extent of the problem, the lack of appropriate policies and approaches, and limited accessibility. This raises the question of introducing emergency and expeditious techniques for provisional care for a large number of paintings scattered among these remote areas. An example from Peru is shown as typical of the methodology and instruments currently in use.

16. On Local Removal of Drying Oil Stains from Paper and Textiles

Nina G. Gerassimova, State
Hermitage Museum, 191065
St. Petersburg, Russia

Old stains of drying and semi-drying oils are difficult to remove from fiber materials due to the oils' conversion into three-dimensionally polymerized linonin which is fixed on fibers. Our studies, carried out with the aim of finding an effective and harmless local technique to remove aged sunflower oil, showed the good cleaning properties of isopropyl alcohol-tetrachloroethylene azeotrope (70:30 by weight) mixed with some starch to make a paste. It is applied locally, up to 3 times, and is removed with a brush after the solvents have evaporated. This technique gives good results on paper and textiles, and seems to work better than using other organic solvents and some industrial cleaning compositions. Among alkaline agents we prefer dimethylaminoethanol in 2% water solution (pH 11.1) which is also used locally with four-layered cotton-gauze and a moderately heated iron when the paper or textile is placed on several sheets of blotting paper.

17. Laser-Based Painting Restoration

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The use of excimer lasers in a variety of painting restoration applications has been examined, and it has been established that the ultraviolet radiation emitted by excimer lasers may induce effective ablation of surface layers of old varnish and/or inorganic and biological materials from paintings in a non-destructive manner. Successful restoration of the original painting from overpaintings and restoration of the canvas or wood substrates have also been demonstrated. The optimization of the laser parameters employed depending on the type of paint materials and surface deposits is discussed. On-line monitoring of the process by reflectivity measurements and image processing techniques ensure the absence of any potential damage.

18. Consolidation of Powdery Paint Using the Ultrasonic Mister

Stefan Michalski, Carole Dignard, Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario, Canada K1A 0C8

A method of subtly consolidating powdery paint using an ultrasonically generated mist has been developed. The advantages of this method over other spray techniques are the small aerosol size, the low mist velocity, the narrow, easily directed stream of mist, and the delivery of aerosol at a known concentration. Penetration is optimized without flooding the surface and smearing is minimal. This method may require several applications of a dilute consolidant solution, such as gelatin in water, methylcellulose in water, Rhoplex AC-33^R in water, Acryloid-B72^R in ethanol, water alone and ethanol alone. Each was tested on 7 different pigment washes on glass and color differences were measured after 1, 4 and 10 applications of 0.5% solutions. Minimal changes in visual appearance can be obtained on the majority of the pigments tested with low concentrations of gelatin or methylcellulose. Certain pigments change in appearance more than others, some simply through wetting with a solvent. Results were found to be similar for pigments on wood, with the exception of ethanol which can cause the wood's resin to migrate and stain the pigment surface. Bond tests were done for three pigments by brushing the surface or by applying blotting paper at a fixed pressure with the conclusion that the paint is stronger after consolidation, but is still delicate. A more controllable approach to consolidation would be to apply a dilute consolidant incrementally to each pigment, monitoring the color change, and stopping either when the bonding is satisfactorily improved, or before the color change becomes unacceptable.

19. The Burgundian and/or Venetian Enamelled Silver Objects of the 15th Century in the Kunsthistorisches Museum in Vienna: A Report of an Interdisciplinary Research Project

Manfred Schreiner, Raleigh Belcher, Wolfgang Baatz, Institute of Analytical Chemistry, Technical University and Academy of Fine Arts, Vienna, Austria; Beatrice Zamora Campos, Kunsthistorisches Museum, Burgring 5, A-1010 Vienna, Austria

The alarming condition of the fully enamelled medieval objects (*émail en ronde bosse*) in the Kunsthistorisches Museum in Vienna led to a study of the degradation process of such artifacts and to elaborate a conservation method to determine their local origins. Analytical investigations carried out using light and scanning electron microscopy with an energy dispersive X-ray analyzing system revealed that the transparent enamel is a high potassium and sodium silicate material. Lead and tin oxides are only present as main elements in the white opaque painted enamel of the artifacts. A marked depletion of Na and K could be detected at the surface of the *émail en ronde bosse*, which indicates that leaching of components has occurred during the centuries and that these objects are highly sensitive to humidity. The varying content of coloring agents can give a hint as to the authenticity of the various artifacts. The results obtained by the scientific investigation are presented.

20. Studies in the Deterioration and Conservation of Historic Glass

Norman Tennent, Department of Chemistry, Glasgow University, Glasgow G12 8QQ, Scotland; Brian Cooksey, David Littlejohn, Carole Morrisson, Department of Pure and Applied Chemistry, Strathclyde University, Glasgow G1 1XL, Scotland

The deterioration of samples of medieval stained glass as a result of cleaning treatments has been investigated. The behavior of medieval samples and glasses designed to simulate medieval compositions has been examined in aqueous solutions of EDTA and distilled water. Five elements (Na, K, Ca, Cu, and Co) leached from the glasses by these solutions have been quantified by atomic absorption spectrometry. For the same glasses, scanning electron microscopy with energy dispersive microanalysis quantified the change in appearance and composition at the glass surface. These results are interpreted in terms of the tendency for glasses of poor stability to undergo deterioration during aqueous conservation treatments. The effects of these simulated cleaning experiments are compared with the observed decay, *in situ*, of some unstable cathedral glasses.

21. The Use of FTIR-Microscopy to Monitor the Effect of Varying Storage Environments on the Physical and Chemical Structure of Glass Surfaces

Naomi Janine Earl Turner, David Watkinson, Archaeological Conservation Section, School of History and Archaeology, University of Wales College of Cardiff, P.O. Box 909, Cardiff CF1 3XU, Wales

A storage system for wet excavated glass during the period before active conservation is proposed. Corrosion occurs in the presence of water and can actually be accelerated in excavated glass during wet storage because alkali ions leached from the glass are unable to disperse. The pH of the storage solution rises until direct attack on the silica matrix occurs. However, storage in a dry, non-aggressive environment is not a possibility because weakened, waterlogged glass cannot be dried out without physical disintegration occurring, since water acts as a consolidant. Various approaches to the storage of archaeological glass are being evaluated. Three simulated glass compositions, one Roman and two Medieval, have been placed in a variety of chemical and physical environments, at ambient or elevated temperatures. The relative effects of the storage systems are being determined principally by FTIR-Microscopy. In glass, the positions of the two peaks detectable by this technique, Si-O-Si and Si-O-X (X=Na, K, Ca, Mg) change in a specific way during corrosion and the systems can be rated accordingly. SEM was used at the start of the experimental period and will be used again at the end to assess the physical effect of the differing storage conditions on the surface. Colorimetry and AAS are being used to quantify the leached ions. A surprisingly short period in the storage environments produced considerable changes in the glass. It seems that it will be possible to select certain storage environments over others. Preliminary results suggest that freezing in ethanol/water mixtures produces little change in the glass. FTIR-Microscopy is proving to be a sensitive analytical tool for monitoring glass corrosion.

22. A Quantitative Study of Decay Processes of Venetian Glass in a Museum Environment

Victoria Oakley, Victoria & Albert Museum, London SW7 2RL, England; Philip Rogers, David McPhail, Jason Ryan, Imperial College, London SW7 2BP, England

The objective of this project is to gain a more precise understanding of the chemical exchange processes at glass surfaces and to monitor the onset of the breakdown process in glass in relation to its environment. The knowledge gained should help to improve the procedures used by conservators for the storage, handling, display, and general care of precious glass vessels. The project is mainly concerned with the characterization of the near surface layers of the glass using sophisticated analysis equipment. Fragments of Venetian glass drinking vessels have been analyzed for their constituents and glasses of the same composition have been prepared in the laboratory. The synthetic glasses have been exposed to a variety of environmental conditions (temperature, humidity, etc.) using controlled-atmosphere chambers, and the surfaces have then been analyzed using secondary ion mass spectrometry (SIMS) and analytical scanning electron microscopy (SEM). Ion implantation techniques have also been used to study the behavior of particular ionic species.

23. Evaluating Historic Restorations in Medieval and Renaissance Stained Glass at the Isabella Stewart Gardner Museum

Valentine Talland Mahanthappa, Isabella Stewart Gardner Museum, 2 Palace Road, Boston, Massachusetts 02115, USA

Incorporated into the design of the Isabella Stewart Gardner Museum is Mrs. Gardner's collection of stained glass windows. Among these windows are six Renaissance panels from the Milan Cathedral and one monumental medieval panel from the Soissons Cathedral in the French region of Reims. All seven panels are scheduled to receive conservation treatment beginning in 1993. In evaluating the condition of the panels, objects conservators at the Gardner Museum have coordinated their examination with experts in the study of European stained glass from the *Corpus Vitrearum*. This cooperative effort has brought to light both the unusually high percentage of original glass as well as the number of historically significant prior restorations in the museum's col-

lection. For both the Milan and Soissons windows, there is substantial documentation of their sequential restoration regimes as well as the individual restorers from the 18th and 19th centuries, such as the ateliers of Didron and Gaudin in France and of the Bertini family in Milan. Their restoration techniques include the use of palimpsest (altered or repainted old glass), cold painting on new and old glass, true enamel color on new glass, and fills of unaltered old glass from other windows. Although some of these restorations are unstable and some are stable but interfere with the interpretation of the panels, some are entirely sympathetic with the overall composition of the windows and are an important part of the windows' history. This poster will illustrate the different types of restorations, identify and describe some of the restorers, and discuss those restorations that have been preserved.

24. The Role of Local Compositional Variations in the Corrosion of Seleucid Glazes from Nippur, Iraq

Blythe McCarthy, Jerome Kruger, Johns Hopkins University, 102 Maryland Hall, Baltimore, Maryland 21218, USA; Pamela Vandiver, Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C. 20560, USA

Trace constituents are commonly found in ceramic glazes due to accidental inclusion, purposeful addition, or nucleation and growth during firing. Their presence causes local variations in composition and microstructure in the surrounding glass. Such heterogeneities are a better indicator of weathering behavior and corrosion rate than bulk composition alone. To determine the role of compositional variations in the degradation process ancient glazes and laboratory replications were examined. The microstructure of three Seleucid glazes was characterized and its effect on corrosion documented using optical microscopy, x-ray diffraction, and scanning electron microscopy with energy dispersive x-ray analysis. Bulk composition was determined using wavelength dispersive electron beam microprobe analysis. Laboratory replications of the glazes were studied during artificial aging with dynamic imaging microellipsometry (DIM), a spatially resolved (50 microns) technique which measures the optical properties of a surface. Changes in the optical properties were correlated to the growth of corrosion layers at the angstrom level. The data from the Seleucid glazes and laboratory studies were used to form an integrated picture of the glaze degradation.

25. Restoration of Textiles from the Esterházy Collection

Katalin E. Nagy, Jenő Rácz, Péter Varga, Anita Magdu, Enikő Sipos, Anikó Pataki, Museum of Applied Arts, Üllői út 33-37, H-1091 Budapest, Hungary

The world-famous collection was founded by Miklos Esterházy in the 17th century. During World War II it was seriously damaged during a bomb attack on the house in Buda Castle where it was kept at the time. The collection was buried under the ruins for four years, causing considerable deterioration of the objects. In 1949, after the pieces had been taken to the Museum of Applied Arts, the textiles underwent a quick cleaning and restoration process. Of the 57 textile objects in the collection, 9 valuable pieces have been restored in the last decade. Restoration of a man's and a child's coat, trappings from the 16th century, and a 17th century felt tablecloth are the subject of the poster. Of particular beauty are the coats which have been embroidered with metal threads. The trappings are a unique piece made of richly embroidered velvet with delicate decorations of gems. The tablecloth is a stuffed embroidery made with gold and silver threads, edged with lace. The general course of restoration consisted of investigation of materials and condition, disassembly, cleaning of the disassembled pieces, reconstruction of missing parts or decorations, support, and reassembly. A representative book on the result of the history, investigation, and restoration of the collection will be published.

26. Analysis of Peruvian Dyestuffs: A Case Study

Arie Wallert, The Getty Conservation Institute, 4503 Glencoe Avenue, Marina del Rey, California 90292; Ran Boyner, Archaeology Program, A148 Fowler Museum, UCLA, Los Angeles, California 90024, USA

Around 1000 AD, two cultural groups, now known as the Tumilaca and Chiribaya cultures, arrived in the Osmore valley in southern Peru. They were initially defined by their ceramic and weaving technology. Chemical and physical examinations of textiles from both cultures were undertaken to gain a better understanding of the dyestuffs and techniques used in an attempt to find possible correlations between dye technology and cultural differences. We tried to identify dyestuff mordants by energy dispersive analysis of X-rays (EDXRF). Dyestuffs were analyzed by the complementary use of UV-visible absorption spectrometry (UVAS), thin layer chromatography (TLC) and a number of microchemical tests. Our analyses showed the presence of various anthraquinone and flavonoid type dyestuffs. Distinct differences were found in the use of dyestuffs and mordants by each culture.

27. Consolidation and Rehousing of Mammoth Collodion Glass Plate Negatives

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Charles Thurston Thompson (1816-1868) was the first head of the Photographic Studio at the Victoria & Albert Museum. His major achievement was to photograph the Raphael Cartoons (property of H.M. Queen) prior to their being placed on permanent loan to the Museum. There are seven cartoons, the largest measuring 11 ft. 4 1/2 in. x 17 ft. 9 1/2 in. A specially constructed camera was used for outdoor photography. In the documentation only three negatives are mentioned; however, in the past three years, 17 mammoth plates have been found. Of these, eleven relate to the cartoons, the remainder to other Museum objects. All of the plates measure 4 feet by 4 feet on Victorian plate glass. A purpose-built cabinet has been made for them and consolidation of the flaking varnish layers will take place in midsummer, 1993. The poster will illustrate the cleaning of the plates prior to making inter-neg master copies, the consolidation of the flaking varnish and emulsion layers, and the rehousing of these objects in a cabinet which assures accessible viewing and a controlled climate. Illustrations and a bibliography will be included.

28. New Approaches in Processing of B&W Photographic Material for Maximum Stability

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In spite of much skepticism, resin-coated (RC) photographic paper is now commonly accepted for making permanent prints. In recent years we have used a standard tray processing procedure for RC-papers followed by a selenium treatment. No detectable residual fixer is left, according to ANSI PH 4.8. To respond to the demand for prints at the Conservation Department we have tested several commercial processors. No processor could make prints to the standard obtainable by the tray processing procedure. However, Ilford Photo A/S, Denmark has made some modifications to an Ilford 2240 RC Processor. A spray bar in the washing tank now irrigates the whole surface of each print with fresh wash water. The dry-to-dry time was lengthened from 70 to 120 seconds which almost doubled the time in each solution, including the wash water. The machine-processed prints now meet the same archival standards as tray-processed prints. The amount of silver converted to selenide and sulfide during the standard selenium stabilizing process depends on the type of negative film or paper. For example, around 10% of the image silver is converted in a Kodak T-max 100 film, compared to 70% for a Kodak Plus x 125 with the same treatment procedure. We propose a modified standard selenium procedure.

29. NARCISSE: Network of Art Research Computer SystemS in Europe

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NARCISSE est un projet européen de recherche et développement fondé par un consortium constitué de quatre institutions culturelles. Il a été créé en mars 1990 dans le cadre de la Direction Générale Télécommunications Industrielles de l'Information et Innovation de la Commission des Communautés Européennes. Ce consortium comporte: le Laboratoire de recherche des musées de France de Paris, les Arquivos Nacionais/Torre do Tombo de Lisbonne, le Rathgenforschungslaboratorium de Berlin et la Banque de Données des Biens Culturels Suisses de Berne. Cette fédération a pour objectif principal la réalisation d'un prototype de banque d'images scientifiques en très haute définition, gérée par une base de données textuelle multilingue en allemand, français, italien, et portugais. Plusieurs millions de documents (photographies et radiographies) des peintures sont conservées dans les institutions culturelles en Europe. NARCISSE répond à un besoin accru de consultation de ces films uniques, fragiles et périssables à court terme. La numérisation en 9 secondes de documents au format A3 avec un scanner à plat adapté à nos besoins réalisé par la société Thomson-Broadcast et l'indexation normalisée des oeuvres ou des documents de laboratoires permettent de les étudier en accès direct, localement ou à distance. Le choix d'une haute résolution (16 points par millimètre de l'oeuvre) et une numérisation à dynamique élevée (36 bits) assurent la pérennité de l'information contenue dans les films. Le stockage est effectué sans perte et avec une compression 16 au format JPEG, sur disque optique numérique ATG de capacité égale à 10G. La base de données multilingue est gérée par un système documentaire relationnel avec recherche multifichier, développé par la société DATAWARE. Un premier CD-ROM multilingue "Art-Science" sur un glossaire illustré d'un choix de mots clés de la base NARCISSE est en cours d'édition.

30. Scientific Analysis of a Group of Carthaginian Ostrich-Egg Funerary Masks

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The group of seven ostrich eggshell masks dating from the 6th to the 3rd century BCE was studied in order to identify their component materials, their means of manufacture, and to distinguish those features which are the result of burial alteration. Microscale features were documented photographically, the pigments, shells, and burial accretions were analyzed, and comparative observations on the structure of the masks and modern ostrich eggs were made. The results show that pigments were applied to the abraded and incised surface of the eggshell fragments using both inorganic and organic colorants. Slight differences in color areas on certain masks have been related to the use of pigment mixtures and/or particle size differences which suggest intentional manipulation of materials for the purpose of achieving specific color relationships. Other colorants used appear to be impure mineral mixtures. During burial a wide variety of diagenetic changes has taken place, including the dissolution and reprecipitation of calcium carbonate, precipitation of manganese oxides from the environment, the possible deterioration of copper-containing pigments and the widespread nucleation and growth of an entirely new phase: hydroxyapatite. This latter phenomenon is perhaps the single most notable feature of the masks today, accounting for a wide variety of surface deposits, decorative layer alterations, and structural changes to the shell itself.

31. Moisture in Wall Painting Deterioration: The Effect of Deliquescent Compounds

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One of the sources of moisture in wall paintings is the absorption of water by deliquescent compounds present in the wall painting structure. To study this effect, calcium nitrate was selected since it is a soluble deliquescent salt frequently found in wall paintings. The thermodynamic and kinetic aspects of the deliquescence process for this salt were investigated in order to establish its role in wall painting deterioration. The environmental conditions under which calcium nitrate undergoes the deliquescence process were checked as a function of the thermohygrometric parameters necessary for controlling such activity. The thermal aspects of the deliquescence process were also investigated by means of differential thermal analysis. The kinetics of the water sorption process was studied for three types of supports on which the salt is deposited—glass, aluminum, and painted plaster—to identify how the support may affect the rate of the deliquescence process. Calcium nitrate tetrahydrate was found to easily deliquesce and crystallize under the environmental conditions typically prevailing for wall paintings and it was demonstrated that in the presence of deliquescent compounds, the wetting of the wall painting surface occurs at relative humidities well below the dew point. Moreover, the rate of deliquescence was found to be higher on the wall painting, and the process to show a thermal effect related to the surface.

32. New Archival Housings Provide Preventive Conservation

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Preservation housings made of a new conservation paper have been shown to significantly reduce deterioration rates in collections of paper artifacts and photographic materials by effectively dealing with both internal and external causes of deterioration. Book pages aged inside the new conservation paper averaged 18.5 folds, a 362% improvement over the pages housed inside acidic housings and 47% better than inside alkaline buffered housings. Photographic negatives were covered with 13 different traditional conservation papers, from during the oxidative gas incubation ANSI IT 9.15 1992 test. Over fifty test cycles were run, and in each case the negative sample protected by the traditional conservation paper was severely damaged. Fourteen different varieties of the new conservation paper were subjected to 116 ANSI test cycles. In each case the specimen negative was totally protected. Similar results have been seen in initial tests with hydrogen sulfide and nitrogen dioxide. The formulations and fiber structures for the new papers are chosen to perform several tasks. Interior layers must readily accept, capture, and neutralize deleterious by-products of deterioration, while the exterior layers prevent oxidative and acid gases in the atmosphere from passing through the paper. Activated carbons are selected which, when combined with alkaline buffers, are effective against many of the dele-

terious compounds we wish to capture and neutralize. Furthermore, a group of alkaline buffers is employed in which pores and molecular cages sized to capture specific molecules have been fabricated. Activated carbon used without alkaline buffers in conservation quality paper was tested, and the performance was essentially identical to the performance of traditional lignin- and sulfur-free alkaline-buffered paper. The non-traditional performance of these new conservation papers offers an advantage in preventive conservation.

33. New Storage at the Royal British Columbia Museum

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An enforced move of the entire Royal British Columbia Museum collection provided the opportunity to upgrade the permanent storage of all artifacts. Everything was moved, from antlers to samplers, and we are proud of the innovative designs we have come up with for storage of our collection. We have applied the best preventive conservation principles in providing artifacts with storage systems that in most cases no longer require direct handling while being withdrawn for study or viewing and protect the artifacts from light, humidity, insect, and earthquake damage. Standardized containers, compacting storage units, and a computerized tracking system have helped us to rationalize the collection and locate artifacts. The poster describes the problems we encountered and solutions we devised for the storage of a number of artifact types within the Biology, Ethnology, and History sections of the Royal British Columbia Museum.

34. Monitoring Packing and Environment for Multi-Venue Loans

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Within the last four years the Victoria & Albert Museum has embarked on an ambitious program of "packaged" loans, involving large numbers of objects (100-150) in a large range of sizes and media, travelling to a number of widely separated venues. The Conservation Department has been active in advising on specifications for packing materials and in monitoring the environment inside and outside the packing cases to test their efficacy. There have been frequent requests to lend paintings on wooden panels. These have been sent and displayed in sealed microclimate cases. Conditions inside and outside the supposedly airtight microclimates have been monitored. If the hermetic seal of these microclimate cases is complete, there is a risk of explosion when there is a substantial pressure drop during air transport. The pressure inside and outside a sealed microclimate case was measured during two air trips (no explosions occurred!). During a recent loan it was proposed that the packing should be altered before the next move, reducing the overall size and weight so that the speed and safety of handling very large cases could be improved. Because this lowered the thermal insulation and shock-damping specifications, temperature, humidity, and vibration levels inside the new lighter cases were measured during handling and transport. This monitoring showed that the previous "over-specification" had been fully justified.

35. Coatings of Zinc Sculptures

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At the beginning of the 19th century, zinc was discovered as a new material appropriate for sculptures and architectural decorations. In this respect, cast and plate zinc were often used to provide a matrix whose appearance could be changed with the aid of coating and paints, making it possible to use zinc to replace other materials. The purpose of this work is to systematize the coatings used on zinc objects and to verify their use by finding examples. The coatings were examined using microscopic, microchemical, and emission spectroanalytical methods, as well as X-ray diffraction. The alloy compositions were determined using atomic absorption spectroscopy. Over the priming, layers of paint were found which are composed of pigments typical of the 19th century. For the media, oils with addition of resins were used. The objects under consideration show similar alloy compositions. Coatings were found which imitate sandstone, marble, wood, bronze, copper, and gold. The appearance of polychrome zinc sculptures is naturalistic.

36. Définition d'une méthodologie pour l'étude de la corrosion des métaux archéologiques: application aux objets en plomb

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37. Delamination and Crack Detection in Wooden Panel Paintings Using Air-Coupled Ultrasound

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38. A New Instrument for Non-Destructive Pixel-by-Pixel Analysis of Art Objects

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39. Pedro Berruguete's Tuchlein "The Last Supper": Materials and Methods of the Artist

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Ce poster porte sur l'étude de la corrosion de matériaux métalliques anciens. La nature variée et la spécificité des objets à conserver sont un handicap pour comprendre les processus de dégradation. Pour s'en affranchir, une méthodologie est proposée. Elle repose sur une vision globale des altérations d'une sélection d'objets, pour limiter les paramètres d'études (nature métallurgique du matériau et/ou environnement corrosif). Elle nécessite l'emploi de techniques scientifiques complémentaires de caractérisation structurale et de composition. L'étude du comportement à la corrosion permet ensuite de définir les surfaces à risque d'évolution et de développer des remèdes de conservation plus adaptés aux cas réels de corrosion. Cette approche est illustrée par l'exemple d'une étude en cours sur la caractérisation des altérations d'objets archéologiques à base de plomb d'époque médiévale.

Determining the physical integrity and structural characteristics of panel paintings is crucial in deciding if works will travel to exhibitions. Air-coupled ultrasound detects flaws that cannot be revealed by more traditional techniques; the capabilities of air-coupled ultrasound are investigated as the technique is able to complement other methods to give a complete analysis of the condition of panel paintings. Air-coupled ultrasound locates delaminations between layers of a painting and cracks at certain angles in the wood without direct surface contact. The technique does not use couplants such as water, grease, or polymers, which are inappropriate for examining art objects. X-radiography, widely used in conservation, does not always show the physical condition of a panel painting completely, nor is it as safe for the operator as ultrasound. An overview of the system will be given, including the experimental set-up, the signal processing, and the inspection configuration. The system is capable of producing two-dimensional representations of paintings. Examples are shown of air-coupled ultrasound detecting delaminations and cracks in both real and mock panel paintings. The support layers are oak, poplar, plywood, and hardboard. The technique's capabilities and limitations in detecting flaws and penetrating a painting's thickness will be listed.

An X-ray spectrometer has been designed for pixel-by-pixel analysis of objects of art and archaeology. The instrument is based on energy dispersive X-ray fluorescence analysis and enables the direct material analysis of artifacts without taking original sample material. Additionally, the elemental distributions along lines and within selected areas can be determined. The characteristic technical data of the instrument are described and results obtained on miniature paintings on parchment and easel paintings are presented.

The acquisition of a large (74" h × 130" w) Castilian painting of the Last Supper (1495-1500) by the Spanish artist Pedro Berruguete and its subsequent treatment provided an opportunity to investigate the methods of this pivotal Renaissance artist. The painting, on four joined pieces of linen, has survived in remarkably good condition with relatively few losses and little overpaint. During its cleaning and stabilization samples of pigment were taken for analysis by X-ray diffraction and polarized light microscopy while infrared spectrophotometry was applied to the analysis of the medium. The results of this investigation show that the artist worked primarily with relatively coarsely ground mineral pigments in a

distemper medium on an unprimed canvas. However, he refined the image by the manipulation of the fineness of these pigments, the application of shadings with lake pigment and the proportioning of opaque and translucent pigments in mixtures used to convey textile surfaces. The deterioration problems noted in the course of the treatment included loss of poorly bound pigment, the darkening of azurite except where protected by the frame, the discoloration of the surface of areas painted in lead-tin yellow and, to a lesser extent, those in lead white, and the darkening of a partially gilt brocade which had been previously restored.

40. Direct On-Column High Temperature GC-MS and Direct Low Voltage Electron Impact Mass Spectrometric Analysis (DEI-MS) of Oils, Waxes, Resins, and Varnishes

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Presently, most methods for paint media analysis rely on extraction, hydrolysis, and saponification in which the compounds of interest are derivatized and characterized by gas chromatography. Although this approach may have advantages, the loss of information about the speciation of the moieties is severe. This applies in particular to lipids in which the fatty acid and alcoholic moieties can combine in many different ways. As an alternative, we have developed an analytical approach in which intact lipids are analyzed directly from the complex sample by thermal desorption and volatilization in combination with mass spectrometry or analyzed by high temperature (HT) GC-MS (up to 450°C) after extraction on a microscale. In the latter case, a derivatization with diazomethane, to methylate free acid groups, and a silylating agent (BSTFA), to protect hydroxyl groups, is performed as a precaution. Waxes, triglycerides, high molecular weight paraffins, pentacyclic triterpenoids, diterpenoids, and their oxidized isomers are well within the range of our HTGC-MS (a Carlo Erba HTGC/SFC 3000 connected to a JEOL DX-303 E/B double focussing mass spectrometer) and in-source direct EI/CI MS over a mass range of 20-2400 Dalton (JEOL SX-102, a reversed geometry double focussing mass spectrometer). The in-source direct MS approach gives unique and characteristic MS fingerprints of waxes, resins, and oils used by artists in the past. The HTGC-MS profiling of the compound mixtures allows a detailed structural assignment of each component. HTGC-MS is especially important for the identification of partially oxidized compounds. Data will be shown on standard compounds and samples taken from oil paintings, wax statues, and an oxidized ancient Egyptian oil.

41. Microgram Scale Characterization of Soluble and Polymeric Components in 17th-Century Oil Paint Samples by Temperature-Resolved Analytical Pyrolysis Mass Spectrometry

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Samples from an oil painting of Rembrandt van Rijn and of Ferdinand Bol, characterized by light microscopy and SEM, were subjected to PYMS analysis. Temperature-resolved analysis revealed the degree of impregnation of the paint film with waxes and varnishes. Data were obtained on polysaccharide, protein, and lipids polymerized in aliphatic networks. The oxidation state of the oil paint film was studied by reactive PYMS under direct transalkylation conditions. Comparative studies were made on samples before and after varnish removal to study the impact of different solvent systems used by Dutch conservators.

42. Analysis of the Binding Media of Rembrandt's "Jewish Bride" Using Pyrolysis - Gas Chromatography/Mass Spectrometry

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As part of a technical study accompanying the recently completed restoration of Rembrandt's "Jewish Bride" at the Rijksmuseum in Amsterdam, binding media were analyzed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Samples were pyrolyzed with tetramethylammonium hydroxide (TMAH), yielding both pyrolysis products and transesterification products. Because aged resins in paint are often largely polymeric, Py-GC may give better results than GC analysis of hydrolyzed and methylated samples. Py-GC/MS analysis of a sample taken from a glaze in the bride's red robe indicated the presence of a drying oil, probably linseed oil, as did a sample taken from an opaque area. Small amounts of diterpenoid resin and beeswax found in both samples may not be part of the original binding medium, as they are ingredients of lining adhesives that have been commonly used in the Netherlands. The top layer of the groom's black hat was soluble in 4:1 white spirit/ethanol and suspected not to be original. Py-GC/MS analysis of samples taken from this layer showed the presence of a variety of materials, among which are paraffin wax, beeswax, diterpenoid resin and dammar resin. No drying oil was found. Further evidence that this layer was a later addition was obtained using optical microscopy and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX) of crushed paint samples and cross-sections. Py-GC/MS analysis of lower paint layers in and around the hat indicated the presence of linseed and walnut oil with traces of diterpenoid resin.

43. The Effects of Solvents on Artificially Aged Egg Tempera Films

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There is little information in the conservation literature on either the aging of egg yolk tempera paint films or on the effects of organic solvents and other cleaning agents on tempera paint films. The present study is an initial investigation of these subjects and focuses on simple observations on reference paint films. Paint films of vermilion, azurite, lead white, verdigris, and films of unpigmented egg yolk medium were subjected to different regimes of accelerated aging. Accelerated aging involved light aging in a xenon arc fadeometer fitted with UV filters, followed by thermal aging in a humidity controlled oven. Samples of aged and unaged films were treated with a range of simple organic solvents: hexane, acetone, toluene, ethanol, and chloroform. Surface topographical changes were monitored using scanning electron microscopy. Compounds extracted by solvent immersion were analyzed by gas-liquid chromatography, as was lipid material remaining in the film. This initial study is being followed by measurements of swelling of the films during and following immersion in organic solvents.

44. Recent Advances in Binding Media Identification Using Multiple Analytical Techniques

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Paint binding media can be complex mixtures of materials and because their identification is often hindered by the presence of pigments and the effects of time, multiple analysis methods may be required for their complete characterization. This paper illustrates the complementary nature of several methods using samples obtained from paintings by Cenni di Francesco and Andrea Mantegna. It includes new aspects developed during the Getty Conservation Institute (GCI) Binding Media Project. Examples for the identification of proteinaceous media include the analysis of cholesterol by gas chromatography/mass spectrometry (GC/MS), phosphorus by energy dispersive analysis (SEM-EDS) and amino acid ratios using gas chromatography and liquid chromatography (HPLC). Infrared mapping microspectroscopy is used to locate and characterize various components in a paint cross-section based on an array of infrared spectra collected from the surface of an embedded paint cross-section. Each analytical method provides important information that, when combined, contributes to a clearer depiction of the sample. A resource collection of reference materials and infrared spectra for binding media will also be discussed.

45. Evaluation of Relative Humidity Effects on Fabric-Supported Paintings by Dynamic Mechanical Analysis (DMA)

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This study reports the first use of Dynamic Mechanical Thermal (DMA) for measuring the effect of moisture on samples of 19th century primed canvas. The samples were provided by the Conservation Department of the Tate Gallery and originally came from the rear of the double-primed canvas of Landseer's "Study of a Lion". DMA was used because it resolves contributions from elastic and viscous components and hence measures viscoelastic parameters of storage modulus (E'), loss modulus (E''), and the ratio of the moduli expressed as $\tan \delta$. The parameters E'' and $\tan \delta$ show maximum values at the glass transition temperature (T_g) and shifts in their peak temperatures are sensitive indicators of the state of the material. Measurements were made on a simple polymeric material (two samples of the copolymer ethylene vinyl acetate containing 18% and 28% vinyl acetate) to illustrate how a shift in T_g , measured as $\tan \delta$, occurs with varying proportions of vinyl acetate. Preliminary DMA investigations of the paint composite samples indicated that it was possible to measure the viscoelastic properties of the material and to measure the changes in the viscoelastic parameters with exposure of the sample to increasing levels of relative humidity (54%, 85%, and 94%). A shift in $\tan \delta$ to lower values of temperature or lowering of glass transition temperature, T_g , was observed. This was accompanied by a lowering in temperature at which the storage modulus E' or the rigidity of the material starts to decrease. These preliminary observations indicate the potential of Dynamic Mechanical Analysis to provide data additional to that obtained from Thermomechanical Analysis. The present study used samples which were 4 mm wide \times 8 mm long \times 3 mm thick and measurements were made in bending mode.

46. Research on the Influence of 19th-Century Silk Weighting on the Accelerated Aging of Silk

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Degradation of fibroin in weighted silk is due to oxidation and hydrolysis of susceptible amino acid residues and hydrolysis of peptide bonds. To determine the extent of the former, a technique was developed to measure the amino acid residues in silk using HPLC. Samples were hydrolysed by 3N HCl at 105°C for 16 hours. The free amino acids were eluted in a gradient of 0.05% trifluoroacetic acid and acetonitrile/propanol (4:1) and separated by means of a C-18 reverse-phase column after derivatization with dansyl chloride. A fluorescence detector was used. In the case of the hydrolysis of peptide bonds, peptides with α -amino groups are released. Preliminary results on developing a technique for the analysis of free N-terminal residues by HPLC after dansyl chloride derivatization are also reported. Prior to the analysis, the method of dissolving the silk had to be optimized. Usual solvent systems were not suitable to dissolve fibroin from weighted silk. Good results were obtained with copper-ethylene diamine. Dialysis for 24 hours was needed to remove the solvent. Results obtained with unweighted aged silk showed that the relative concentration of the amino acid residues changed after aging. To determine the influence of the weighting materials on the degradation of silk, further experiments will be done with self-weighted silk.

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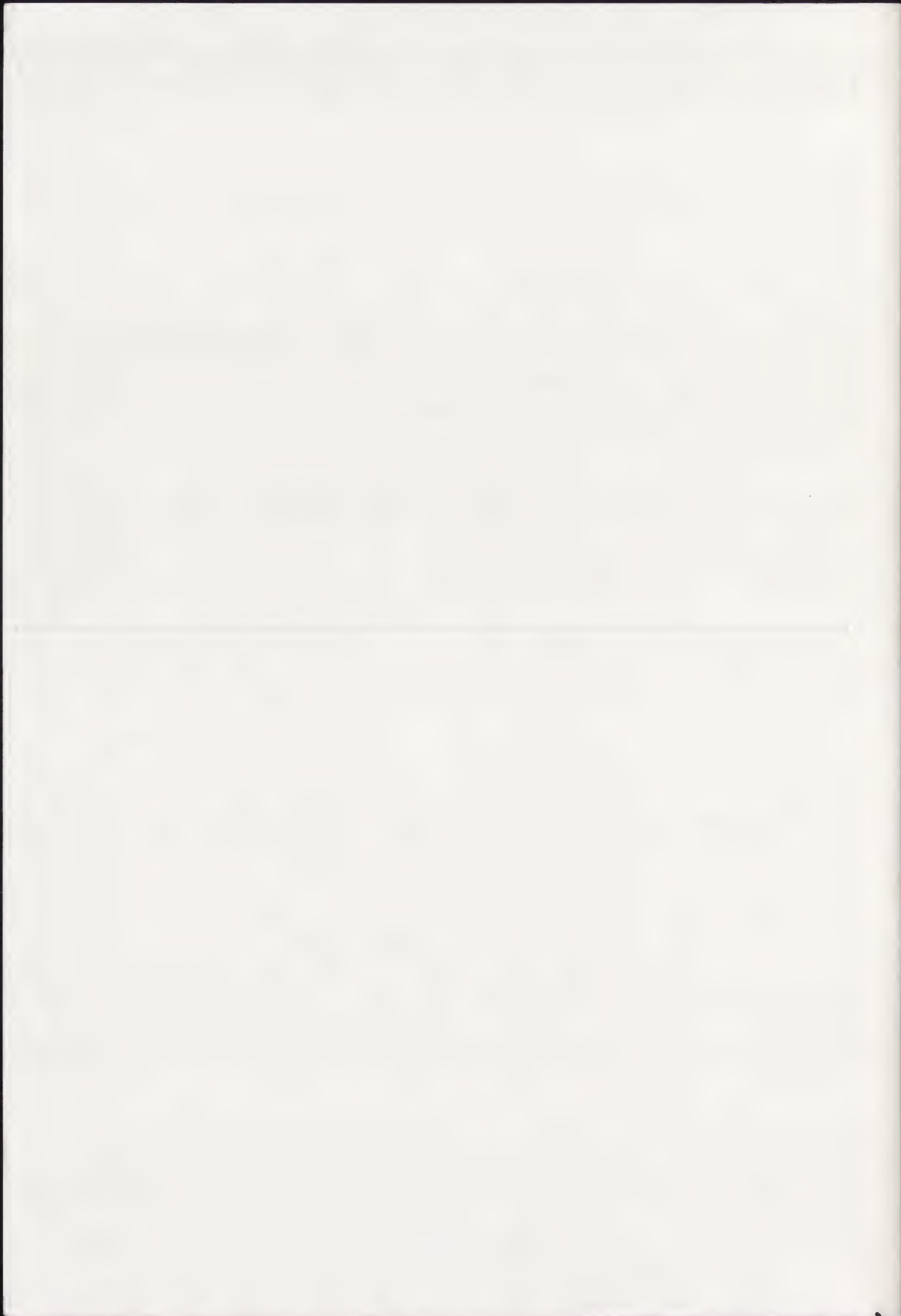
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